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CORRECTION

Canadian Journal of Chemistry, Vol. 35, p. 915. The portion two inches down from the heading on the right side of Table I should read:

	1794		
1802 ms	1800	A	$785 + 1030 = 1815 (A_1)$
	1807		
	1851		
1858 ms	1861	B	$785 + 1081 = 1866 (B_1)$

REFERENCES—CANADIAN JOURNAL OF CHEMISTRY

This is to announce a change from the present system of citing references. Beginning in January 1958, references will be numbered and listed in the order of first citation in the text, not in alphabetical order by authors' names. Authors are requested to follow the new system in all manuscripts submitted henceforth.

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THE EFFECT OF HYDROGEN CHLORIDE ON THE INFRARED SPECTRUM OF NYLON¹

P. LAROSE

ABSTRACT

The effect of HCl on the infrared spectrum of nylon in the form of Zytel films was studied in the region 3600 cm.⁻¹ to 600 cm.⁻¹. The effect of partial deuteration of the films was also observed. Definite changes in the characteristic bands of the NH—CO group show that HCl interacts with this group. The results indicate that the two NH bands at 3300 cm.⁻¹ and 3030 cm.⁻¹ are associated with different NH bonds. The general effect of the HCl seems best explained by assuming a polar interaction with the peptide linkage. The behavior of several of the bands is readily explained on the basis of the picture given by Fraser and Price for the NH—CO vibration.

INTRODUCTION

Experiments in which the sorption of hydrogen chloride by nylon was measured have shown that nylon is able to sorb large quantities of this gas (9). From the results of these experiments it was concluded that hydrogen chloride was interacting with the amide linkage —NH—CO—, either by forming hydrogen bonds with it or by a double pole association with the charged group



the sorption of hydrogen chloride to be accompanied by a change in the infrared spectrum of the nylon. Accordingly the spectra of nylon films which had sorbed hydrogen chloride under various conditions were examined. Although the results have thrown little light on the mechanism of sorption owing to the uncertainty in the interpretation of some of the original nylon bands, they are considered of sufficient importance to report at this time. In an attempt to learn more about the changes taking place during the sorption of hydrogen chloride by nylon, the infrared spectra of nylon treated with DCl, with D₂O, and with CH₃OD were also examined.

EXPERIMENTAL

It was not possible for us to examine the infrared spectrum of the nylon fibers which had been used in our previous sorption experiments, for our equipment did not have a microscope attachment. Thin films were therefore prepared by casting on glass from solutions of "Zytel" in ethyl alcohol. Analysis showed that the Zytel used was a copolymer of nylon 6, nylon 6-6, and nylon 6-10 in the approximate proportions of 40:30:30. This polymer is readily soluble in ethyl alcohol.

The films were readily removed from the glass by water. For exposure to HCl, the films were mounted on small cardboard frames having a circular opening with a diameter

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slightly larger than that of the NaCl plates between which they were placed for examination in the spectrometer. The spectra were obtained in a Perkin-Elmer, Model 21 double beam instrument with rock salt prism, and the range $3800\text{--}600\text{ cm}^{-1}$ was usually covered.

Spectra of the films treated as follows were examined:

- (a) Untreated film.
- (b) Film exposed to HCl for 10 minutes only.
- (c) As in (b) and with HCl removed by evacuation.
- (d) Film exposed to HCl for several hours.
- (e) As in (d) and with HCl partially removed by evacuation.
- (f) Film left in contact with D_2O for several hours and dried in desiccator.
- (g) Film treated with DCl for 10 minutes.
- (h) Film treated overnight with DCl.
- (i) Film cast from solution in CH_3OD and removed with H_2O .
- (j) Film cast from solution in CH_3OD and removed with D_2O .

All treatments were carried out at room temperature. Earlier experiments had shown that the sorption apparently takes place in two stages, the first stage being a rapid one occurring within a few minutes, while the second stage is a slow one which extends over several hours or even days, depending on the conditions; hence the reason for (b) and (c), and (g) and (h).

RESULTS

Figs. 1-6 show the spectra for some of the most important nylon bands. The main changes observed as the result of the various treatments to which the Zytel films were submitted are as follows:

3300 cm^{-1} and 3080 cm^{-1} Bands

These bands are generally attributed to the N—H bond. The 3300 cm^{-1} band is recognized as a stretching vibration of the valence bond but the significance of the 3080 cm^{-1} band is a subject of controversy. On HCl sorption these two bands become fused into a broad band (Fig. 2). While the intensity of the 3300 cm^{-1} band is greatly reduced, that of the 3080 cm^{-1} band appears unchanged. The peak of the first band is now at 3230 cm^{-1} while the position of the other band seems to have changed little, if any. After the sample has been freed of as much HCl as possible by evacuation, the original bands reappear but with some change (Fig. 3). The 3300 cm^{-1} band has its peak at 3275 cm^{-1} and its intensity is reduced appreciably, while the 3080 cm^{-1} band has greater intensity than before, relative to the CH_2 bands. Owing to difficulty in obtaining films of uniform thickness, the CH_2 bands have been used as reference points to compare the intensities although the intensity of the antisymmetric 2940 cm^{-1} vibration appears somewhat reduced on HCl sorption, but not the symmetric 2870 cm^{-1} band.

The main difference between the spectrum of the film (b) exposed to HCl for a short time and that of (d) submitted to a long exposure to the gas is that the bands are not so clearly defined or so pronounced in (d) because of intense background, probably due to scattering. The remarks will therefore be limited to film (b) although the changes in (d) appeared to be of the same kind.

The changes occurring when DCl is sorbed are practically the same as those observed when HCl was used (Fig. 4). In this case, however, the results of long exposure to the gas were identical with those obtained after a short exposure. With DCl the N—H bands

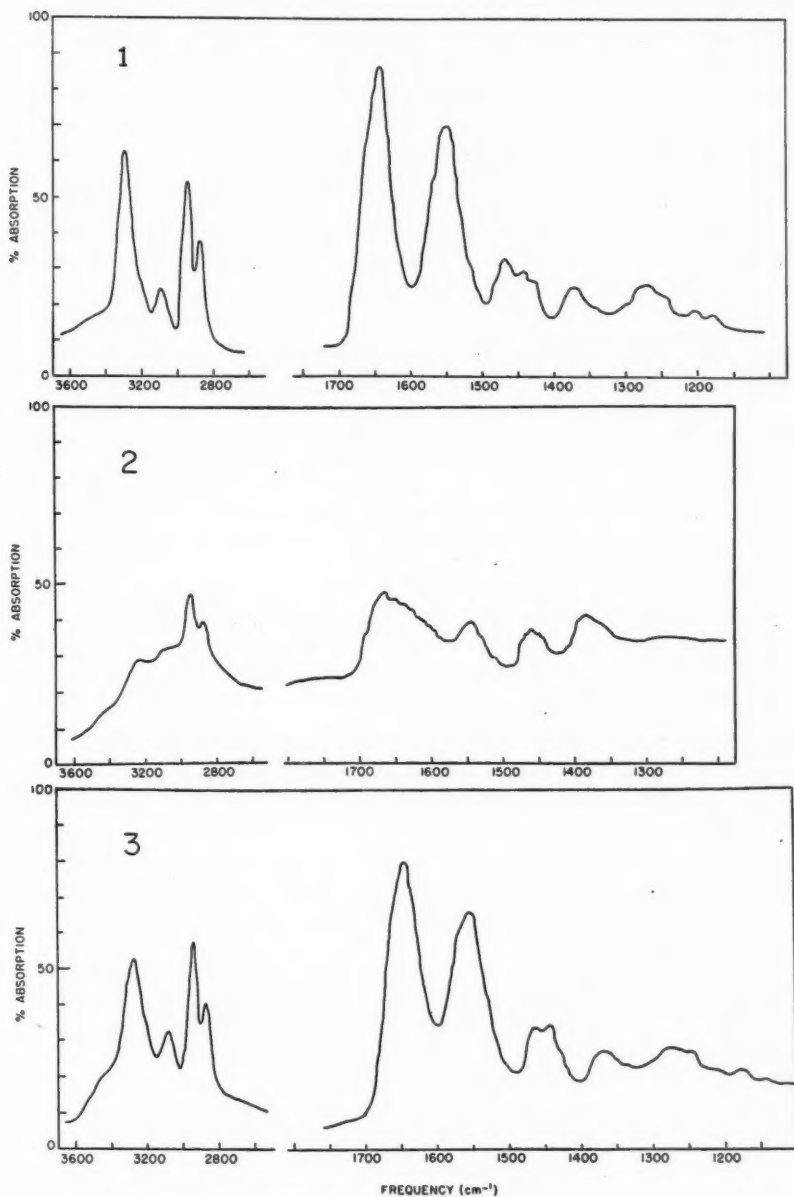


FIG. 1. Infrared spectrum of untreated Zytel film.

FIG. 2. Infrared spectrum of film after short exposure to HCl.

FIG. 3. Infrared spectrum of HCl-treated film after removal of the HCl.

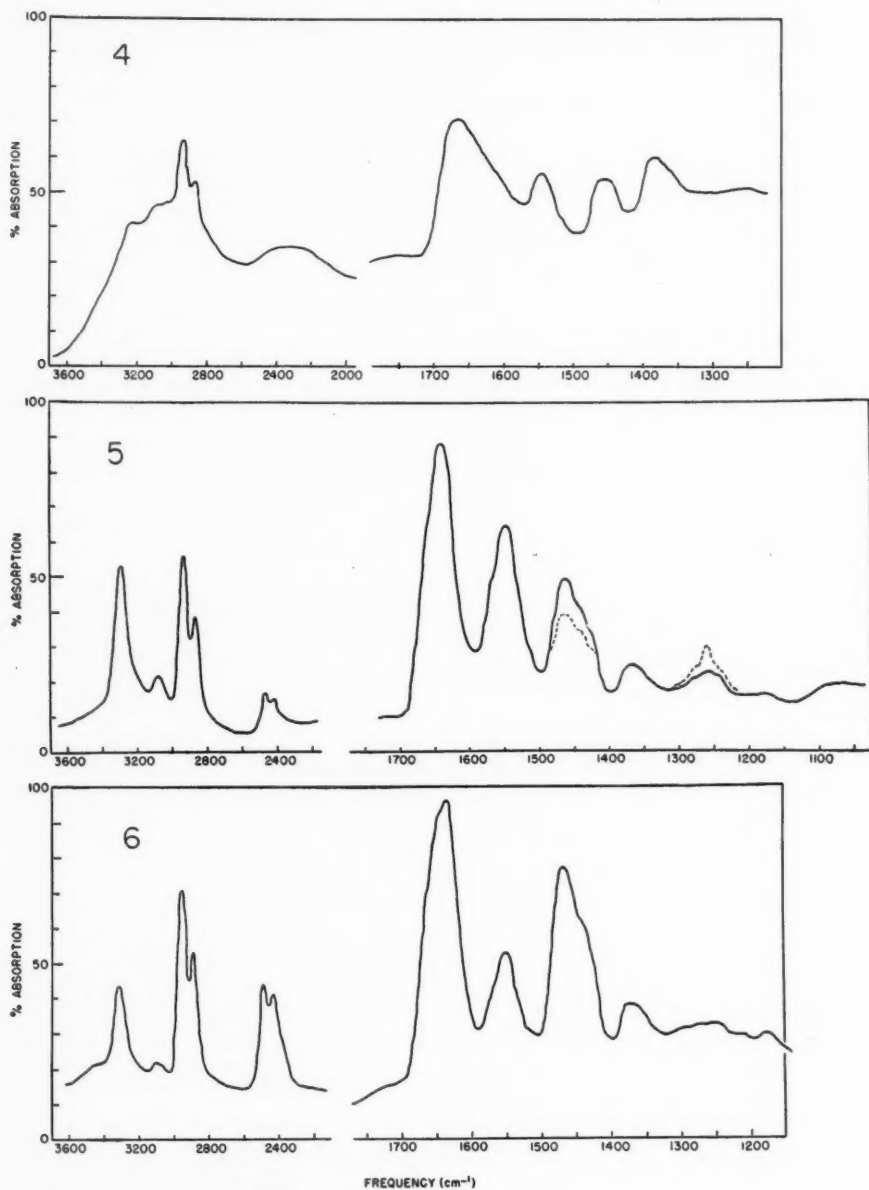


FIG. 4. Infrared spectrum of film treated with DCl.

FIG. 5. Infrared spectrum of film treated with D₂O. Full line = 6 hours treatment at room temperature. Dotted line = 4 days treatment at room temperature.

FIG. 6. Infrared spectrum of film cast from a CH₃OD solution and removed with D₂O.

are better separated than with HCl and it is possible to place the peak of the second N—H band originally at 3080 cm^{-1} at 3060 cm^{-1} . This gives a shift of the same order as that of the original 3300 cm^{-1} band. In the spectrum of the films treated with DCl, there is also a wide band of low intensity at $2400\text{--}2200\text{ cm}^{-1}$ which is more pronounced than in the spectra of the other films.

The treatment of Zytel films with D_2O gave rise to some new bands as expected (Fig. 5). Two bands at 2480 cm^{-1} and 2420 cm^{-1} must correspond to the deuterated N—H band at 3300 although it is difficult to see why there should be two such bands. The ratio $3080/2420 = 1.27$ seems too low to explain the 2420 cm^{-1} band as a deuterated 3080 cm^{-1} band. The two bands have also been found at 2530 cm^{-1} and 2480 cm^{-1} in deuterated polyglycine (3), and in certain amides at 2450 cm^{-1} and 2410 cm^{-1} (11) and at 2420 cm^{-1} and 2380 cm^{-1} (1). The treatment of the films with D_2O was carried out at room temperature. At this temperature the replacement of the hydrogen is only partial and the intensity of the original N—H bands remains quite high, even after a 4 day treatment.

Deuteration was also effected by dissolving the Zytel in CH_3OD and removing the cast film with D_2O (Fig. 6). Removing the film with ordinary water produced little change since the water apparently reversed any deuteration effected by the alcohol. The deuteration by CH_3OD proceeded to a greater degree than that observed with D_2O but the two new bands are at 2480 cm^{-1} and 2420 cm^{-1} as with D_2O .

1645 cm^{-1} Band

The 1645 cm^{-1} band, generally attributed to the C=O bond, becomes much broader when a Zytel film sorbs HCl (Fig. 2). The peak of the band shifts to a frequency of 1665 cm^{-1} , but a number of smaller auxiliary peaks appear on the low frequency side of the band. There is also a noticeable shoulder at about 1690 cm^{-1} . When the HCl is removed the original band reappears (Fig. 3) with only a slight drop in intensity. There are several faintly discernible shoulders on this band as well as on the original band. These are approximately at 1660 , 1652 , 1635 , 1628 , 1625 , and 1617 cm^{-1} .

The effect of DCl is about the same as that of HCl except that the intensity is relatively higher.

Treatment with D_2O produces no pronounced change in the C=O band but deuteration by CH_3OD shifts the peak to a frequency of 1635 cm^{-1} , and the 1645 cm^{-1} band now appears as a shoulder a little below the 1635 cm^{-1} peak.

1550 cm^{-1} Band

The 1550 cm^{-1} band, often referred to as the amide II band, has its maximum shifted to 1542 cm^{-1} as the result of HCl sorption, and has its intensity diminished. The 1550 cm^{-1} band, like that at 1645 cm^{-1} , has a number of discernible shoulders at 1577 , 1567 , 1542 , 1537 , 1528 , 1522 , and 1517 cm^{-1} , some of which are missing from the spectrum of the film with HCl but which reappear when the HCl is removed. Removal of the HCl accentuates some of these bands.

The effect of DCl is similar to that of HCl.

The D_2O treatment did not produce any appreciable change in the appearance of this band but treatment with CH_3OD reduced its intensity by about 50%. However there was no displacement of the band.

1450 cm^{-1} Band

This is a complex broad band which shows two distinct maxima at 1470 cm^{-1} and

1440 cm^{-1} and a shoulder at about 1430 cm^{-1} . Quynn (10) shows a spectrum with a double band at 1440 cm^{-1} and 1430 cm^{-1} , while a spectrum given by Holliday (7) has a band at about 1460 cm^{-1} with a shoulder at 1430 cm^{-1} . This might be the same band observed at 1450 cm^{-1} in polyethylene (13) and attributed to a CH_2 deformation mode. It was also observed at 1440 cm^{-1} in glycine peptides (3). On HCl sorption this band shows a main peak at 1460 cm^{-1} , while after desorption of the HCl, it appears with two peaks at 1462 cm^{-1} and 1440 cm^{-1} , and with little change in intensity. DCl treatment results in a band with a broad flat peak between 1465 and 1440 cm^{-1} .

The effect of D_2O is anomalous in that a short treatment (6 hours) gave a band with higher intensity (Fig. 5, full line) than the treatment lasting several days (Fig. 5, dotted line).

Deuteration with CH_3OD has a pronounced effect on the intensity of this band (Fig. 6). Whereas the original band had an intensity of about half that of the 2940 cm^{-1} band in optical density units, after deuteration, its intensity was higher than that of the CH_2 mode used as reference.

1370 cm^{-1} Band

This band appears at about 1390 cm^{-1} in the spectrum for nylon given by Holliday (7) and at about 1380 cm^{-1} in the spectrum shown by Quynn (10). In the spectrum for acetanilide, Abbott and Elliott (1) report a band at 1325 cm^{-1} which they attribute to a deformation mode of the N—H bond. In the spectra of the Zytel films, deuteration does not affect this band; the only noticeable change is a shift to a higher frequency of 1385 cm^{-1} on HCl sorption with some increase in intensity, but on removal of the HCl the original band reappears with practically the same intensity and same position it had before the sorption of HCl.

1270 cm^{-1} Band

This band also appears at 1270 cm^{-1} in the spectrum given by Quynn (10) for nylon and at about 1290 cm^{-1} in that given by Holliday (7). The band disappears almost completely when a Zytel film sorbs HCl (Fig. 2) but reappears with little change when the HCl is removed. Whereas the original band, which is quite broad, has a shoulder at about 1245 cm^{-1} , the band after HCl removal from the film appears with two peaks at 1275 cm^{-1} and 1250 cm^{-1} . The effect of DCl is similar to that of HCl. Deuteration with D_2O shifts the maximum of the band to 1260 cm^{-1} (Fig. 5) and the peak becomes quite sharp with prolonged exposure (dotted line), but deuteration with CH_3OD has quite a different effect (Fig. 6). Here the intensity is greatly reduced and the band is wide and flat, although it still shows a maximum around 1250 cm^{-1} .

Bands around 1200 cm^{-1}

Two small bands appear at 1200 cm^{-1} and 1175 cm^{-1} in the original Zytel spectrum. These bands can also be found in the nylon spectra of Quynn (10) and of Holliday (7). The 1200 cm^{-1} band disappears when HCl is sorbed by the Zytel film while the 1175 cm^{-1} band appears only as a slight rise against the background. When the HCl is removed from the film the 1175 cm^{-1} reappears, but there is no sign of the 1200 cm^{-1} band. DCl has the same effect as HCl, and deuteration with D_2O also produces a similar spectrum in this region. Deuteration with CH_3OD again causes the 1200 cm^{-1} band to disappear but the 1175 cm^{-1} band does not seem to be affected.

A thick film of Zytel ($\sim 40 \mu$) showed several peaks in the 600–1200 cm^{-1} region but on HCl sorption the background intensity was so high that it was impossible to

study the changes taking place in this region. Bands at 1120, 1076, 1030, 975-960, 930, 825, 730-675 cm^{-1} were clearly defined in the spectrum of the thick film.

DISCUSSION

It is evident from the changes produced in the infrared spectrum of Zytel when HCl is sorbed that there is interaction with the NH-CO linkage. This is reflected by a change in the NH bands and in the C=O band. However these changes are not readily interpreted since the exact significance of some of the bands, notably that at 3090 cm^{-1} and the amide II band at 1550 cm^{-1} , is not too well known. These are therefore of little help in arriving at some decision regarding the mechanism of the interaction between the HCl and the peptide linkage.

The small shift in the bands would indicate that no hydrogen bonds are broken, but the possibility of hydrogen bond formation with the HCl is not ruled out since this would mean simply the replacement of one hydrogen bond by others of slightly different strength. Salt formation with $>\text{NH}$ to give $>\text{NH}_2^+ \text{Cl}^-$ seems unlikely since there are no new bands attributable to $>\text{NH}_2^+$ in the HCl-treated samples. Moreover there would be a greater shift in the C=O band because of the disappearance of the hydrogen bond between it and the $>\text{NH}$.

Polar interaction appears to be the most plausible explanation for the behavior observed. It would explain the broadening of the bands when HCl is sorbed, and the change in environment could readily account for the small shifts observed. The changes in intensity are more difficult to explain. One would expect a dipole-dipole interaction between $\begin{smallmatrix} + & - \\ \text{NH} & \text{CO} \end{smallmatrix}$ and $\begin{smallmatrix} + & - \\ \text{H} & \text{Cl} \end{smallmatrix}$ to accentuate the polarizability of the peptide linkage and therefore to increase the intensity of the bands contrary to the results obtained. On the other hand the HCl may be regarded as a diluent of high dielectric constant which would reduce the effective charge on the NH-CO group and thus reduce the interchain interaction.

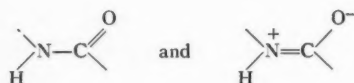
In this connection it may be pointed out that according to Cannon (4), the interchain forces in polyamides are polar in nature and that dipole interaction between the CO-NH groups rather than hydrogen bonding holds the chains together.

One of the most important observations made is the behavior of the 3080 cm^{-1} band as compared with that of the 3300 cm^{-1} band, when HCl is sorbed by Zytel films. One must conclude from this observation that there are two types of N-H bonds, of which only one is affected by the HCl. The significance of the 3080 cm^{-1} band has been discussed by Bellamy (2) and by Quynn (10) and the various explanations given for it need not be repeated here, but it may be recalled that Darmon and Sutherland (5) had interpreted the two bands at 3280 cm^{-1} and 3060 cm^{-1} found in proteins and in peptides as due to two different types of hydrogen bonds. Sutherland's second explanation (12, p. 278) that the two bands arise from a frequency interaction between identical NH bonds is not in accord with the results of our experiments. In this connection, it should be noted that, on deuteration, the 3080 cm^{-1} band does not appear to give rise to a corresponding ND band which might be expected around 2260 cm^{-1} . Holliday (8) also observed a difference in behavior of the 3050 cm^{-1} and 3300 cm^{-1} bands when nylon was heated. Whereas the frequency of the 3300 cm^{-1} band shifts to higher wave numbers, there is no shift in the 3050 cm^{-1} band.

It should be emphasized at this point that in HCl sorption, the crystalline regions as well as the amorphous regions of nylon are affected. This has been shown by X-ray

studies we have made (unpublished). It is also indicated by the large amount of HCl which nylon can sorb (9).

The 1645 and 1550 cm^{-1} bands represent, according to Fraser and Price (6), two modes involving both C—N and C=O bonds and result from the mechanical interaction between the vibrations of the two bonds. Since resonance is presumed to take place between the two structures



it is evident that the introduction of a polar gas such as HCl will disturb this equilibrium and thus alter the relation between the two modes in question. If the effect of the HCl is similar to a weakening of the H bonds, then the shift in the 1550 cm^{-1} mode, mostly a deformation mode, to lower frequencies, and a shift of the C=O mode, a stretching vibration, to higher frequencies would be readily explained. However, the shift of the 3300 cm^{-1} band to lower frequencies would indicate a strengthening rather than a weakening of the hydrogen bonding effect.

On deuteration, the 1550 cm^{-1} band has diminished intensity but there appears to be no corresponding ND deformation band which Abbott and Elliott (1) placed at 980 cm^{-1} in the spectrum of acetanilide.

The coupling between the NH deformation mode and the NCO vibration mode does not occur after deuteration so that one would expect the NCO mode given by Fraser and Price at 1460 cm^{-1} to be in evidence. This is no doubt the reason for the great increase in the intensity of the band we have found at 1465 cm^{-1} (Fig. 6) in the film cast from a CH_3OD solution. This band, although much weaker, was also present in the original Zytel spectrum at 1470 cm^{-1} but moved to 1460 cm^{-1} when HCl was present and remained in that position after the HCl was removed. The effect of HCl on the N·C·O band might be expected to be small. The other two bands at 1440 cm^{-1} and 1430 cm^{-1} are not so readily identified. Abbott and Elliott (1) observed a band at 1436 cm^{-1} in the spectrum of acetanilide, which they associated with the C=O bond, but there is no evidence of such an association here, for either the 1440 cm^{-1} or the 1430 cm^{-1} band. The CH_2 deformation bands are in this region, but deuteration would not be expected to change such bands. It is quite possible that the CH_2 deformation bands are those observed in the spectrum of the untreated film and that they are superposed onto the NCO band of the deuterated sample. However there is a band at 1370 cm^{-1} which does not appear to be associated with either the NH or the C=O bond, since it is little affected by the HCl or by deuteration. This may well be a CH_2 deformation mode although it is at a lower frequency than that usually assigned to such vibrations.

Fraser and Price (6) have postulated a band at 1270 cm^{-1} to represent the in-phase component of the coupling between the C—N vibration and the NH deformation vibration, the mode being mostly determined however by the C—N vibration. If this explanation is correct, this band should behave somewhat like the 1545 cm^{-1} band and in fact in the spectra we observed, the intensity changes of the 1270 cm^{-1} band appear to follow those of the 1550 cm^{-1} band, due consideration being given to the fact that its initial intensity is much lower than that of the 1545 cm^{-1} band.

The bands at 1200 cm^{-1} and 1175 cm^{-1} are of so low intensity and the spectra so indefinite in this region that further discussion of these bands would not be justifiable.

Further studies which are planned with oriented filaments and an examination of the changes in dichroism resulting from HCl sorption will no doubt give us more information on the interaction of HCl with the peptide bond.

ACKNOWLEDGMENT

The author is greatly indebted to Mr. R. Lauzon for his assistance in recording the infrared spectra of the various films studied.

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CINÉTIQUE DE L'HYDROLYSE DE L'ADÉNOSINE TRIPHOSPHATE EN SOLUTION ALCALINE¹

A. M. COUTURE ET LUDOVIC OUELLET

RÉSUMÉ

La cinétique de la réaction d'hydrolyse de l'adénosine triphosphate en milieu alcalin a été suivie à des températures voisines de 90° C. Le taux de la réaction à des pH allant de 8.3 à 9 peut s'exprimer par la relation

$$-d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+]$$

où

$$k = (eRT/Nh)\exp(39.2/R - 29200/RT).$$

INTRODUCTION

L'hydrolyse de l'adénosine triphosphate (ATP) est une des réactions biochimiques importantes. Elle est reliée à un grand nombre de réactions métaboliques et au problème de la contraction musculaire (12). L'hydrolyse de l'ATP par la myosine a été étudiée par plusieurs groupes de chercheurs et semble un cas simple de catalyse enzymatique (9).

Friess (4) a publié des résultats sur l'hydrolyse de l'ATP et de quelques autres substances similaires en milieu acide (pH près de 1) et a trouvé une enthalpie d'activation de 20.6 kcalories/mole et une entropie d'activation de -17.4 unités d'entropie. L'interprétation de ces résultats est compliquée par le fait que la charge ionique de l'ATP dans ces conditions n'est pas bien définie (1).

Parce que l'hydrolyse de l'ATP en présence de myosine se fait à un pH supérieur à 7 et aussi parce que dans ces conditions l'ion est porteur de quatre charges négatives ($pK_a = 6.95$) et que l'effet de la température sur la constante d'ionisation est faible il serait utile d'avoir de plus amples renseignements sur l'hydrolyse alcaline de cette substance.

PARTIE EXPÉRIMENTALE

Réactifs

Le sel de potassium de l'ATP a été utilisé pour ce travail expérimental (Pabst Laboratoires, Milwaukee, Wis.).

Façon de procéder

Toutes les réactions furent étudiées en solutions tamponnées (borate de sodium - acide borique) ou en présence de soude dans des récipients de verre Pyrex fermés par des bouchons de verre rodés. La force ionique (μ) du milieu d'hydrolyse était ajustée par l'addition de chlorure de sodium. La majeure partie (90-95%) de la solution, contenant ce tampon, était incubée pendant une heure dans un bain à température constante ($\pm 0.05^\circ \text{C}$). Ensuite la quantité nécessaire d'ATP, gardée à une température plus basse, était ajoutée et mélangée. Des échantillons de 5 ml. étaient retirés à des intervalles de temps mesurés et étaient analysés pour l'ion orthophosphate d'après une méthode colorimétrique proposée par Fiske et Subba Row (3), utilisant un spectrophotomètre du type Beckman, modèle DU.

¹Manuscrit reçu le 2 juillet 1957.

Contribution du Département de Chimie de l'Université d'Ottawa, Ottawa, Canada, avec l'aide financière du Conseil National des Recherches.

Le pH des solutions tamponnées était calculé à partir de données sur la variation de la constante de dissociation de l'acide borique (6). Les solutions d'ATP étaient complètement neutralisées ($\text{pH} > 8$) avant d'être mélangées à la solution tamponnée pour une réaction donnée.

RÉSULTATS

Nature de la réaction

Afin d'établir la nature de la réaction, une solution d'ATP (10^{-3} M.) fut laissée une semaine à 50°C . en présence de potasse décimale. La composition de la solution, déterminée d'après la méthode de Cohn et Carter (2), adsorption sur Dowex-1 et élution par des solutions de différentes forces ioniques, étaient approximativement: adénosine triphosphate, 0.46×10^{-3} M., adénosine diphosphate (ADP), 0.35×10^{-3} M., acide adénylique, 0.11×10^{-3} M., adénosine, 0.03×10^{-3} M., et adénine 0.04×10^{-3} M. Il semble donc justifié de supposer que la première étape de la réaction est



La variation de la concentration de phosphate avec le temps au début de la réaction correspond donc au taux d'hydrolyse de l'ATP. Plus tard, la réaction deviendrait compliquée par l'hydrolyse successive des produits de l'étape initiale.

Ordre de la réaction

La réaction à des températures voisines de la température ambiante est extrêmement lente en milieu alcalin. La réaction fut donc suivie aux environs de 90°C . et à des températures quelque peu inférieures.

Le taux de la réaction, défini comme le nombre de moles de phosphate produit par seconde, ne semble pas varier avec le temps dans les diverses conditions où la réaction a été étudiée (figure 1).

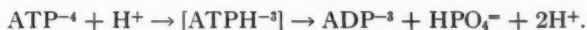
Cependant le taux de réaction augmente linéairement avec la concentration de l'ATP (figure 2). L'ordre déterminé d'après la méthode différentielle est 1.0 par rapport à l'ATP. Ces résultats sont semblables à ceux de Friess (4).

L'influence du pH sur le taux de la réaction est plus complexe. Pour des concentrations de soude variant de 0.02 à 0.1 N, à force ionique constante ($\mu = 0.106$) le taux de la réaction ne varie que de 25%. En utilisant un tampon au borate, à des pH allant de 8.3 à 8.8, on obtient un taux décroissant avec une augmentation de la concentration des ions hydroxyle. Tel que montré dans la figure 3, le taux augmente linéairement avec la concentration des ions hydrogène, et l'ordre de la réaction obtenu par la méthode différentielle est 1.0 par rapport aux ions hydrogène. L'expression empirique

$$[2] \quad -d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+]$$

décrit donc de façon adéquate la cinétique de l'hydrolyse de l'ATP dans cet intervalle de pH.

Ces données semblent indiquer que le complexe activé se forme et se décompose d'après le mécanisme suivant:



L'hydratation des ions semble jouer un rôle important également. Cependant c'est un rôle difficile à élucider en solution aqueuse.

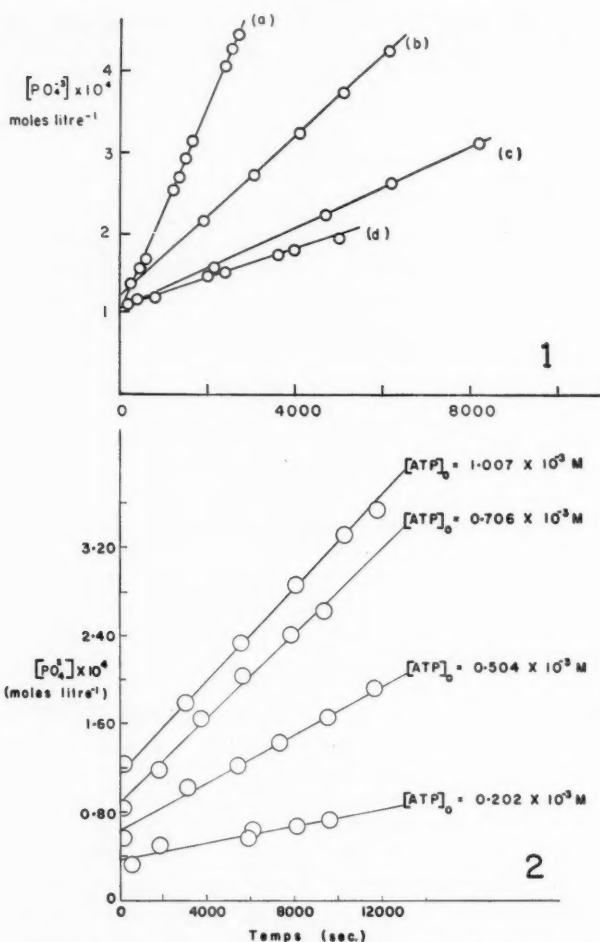


FIG. 1. Variation de la concentration, en moles par litre, de phosphate inorganique en fonction du temps durant l'hydrolyse d'une solution 0.001 M. d'ATP; (a) pH 8.05, $\mu = 0.106$, 90° C., (b) pH 8.82, $\mu = 0.7$, 90° C., (c) en présence de soude décimale, $\mu = 0.106$, 90° C., (d) pH 8.82, $\mu = 0.106$, 84.6° C.

FIG. 2. Influence de la concentration initiale de l'ATP sur le taux de la réaction d'hydrolyse.

Énergie d'activation

L'influence de la température sur le taux de la réaction a été étudiée en présence de soude décimale et dans un tampon à pH 8.82. La figure 4 montre le graphique obtenu en portant dans les deux cas le logarithme de la vitesse en fonction de l'inverse de la température Kelvin. L'énergie d'activation est 29.0 kcalories/mole en présence de soude décimale et 29.2 kcalories/mole à pH 8.82. L'entropie d'activation, ΔS^\ddagger , obtenue de la relation d'Eyring (5),

$$[3] \quad k = (eRT/Nh)\exp(\Delta S^\ddagger/R - E_a/RT),$$

est 39.2 u.e. par mole de complexe activé, à pH 8.82.

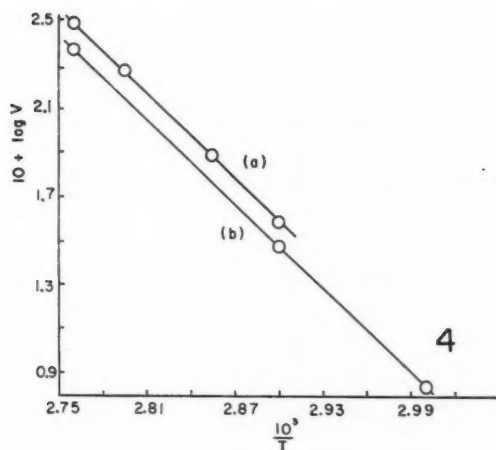
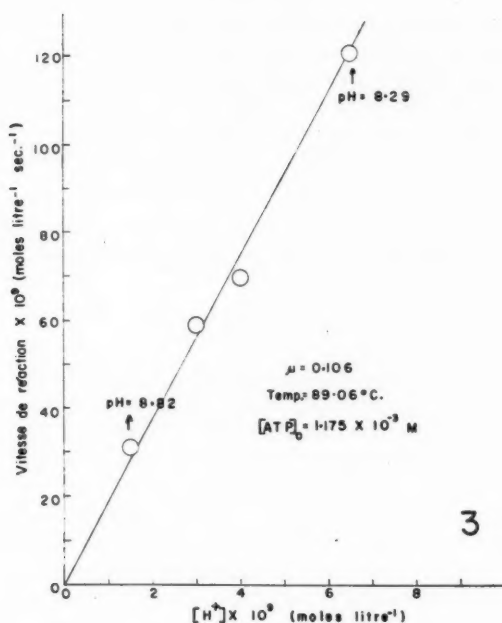


FIG. 3. Influence de la concentration des ions hydrogène sur le taux d'hydrolyse de l'ATP à des pH variant de 8.2 à 8.9.

FIG. 4. Variation du logarithme du taux de la réaction V en fonction de l'inverse de la température Kelvin pour l'hydrolyse de l'ATP (a) à pH 8.82, (b) en présence de soude décimale.

DISCUSSION

Il est intéressant de comparer les résultats sur l'hydrolyse de l'ATP catalysée par les ions hydrogène en solution alcaline aux résultats obtenus dans le cas d'autres réactions entre ions. Wynne-Jones et Eyring (13) ont déjà montré que les effets électrostatiques lors du rapprochement de deux ions de charge Z_a et Z_b amèneraient un changement d'entropie

$$[4] \quad \Delta S = (Z_a Z_b e^2 / Dr) (\partial \ln D / \partial T)_p$$

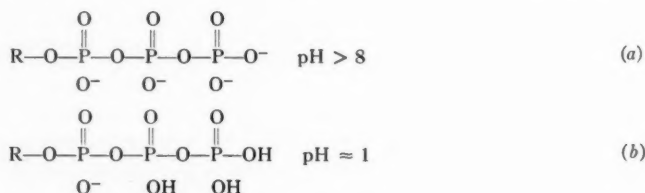
où D est la constante diélectrique du milieu, e la charge de l'électron et r la distance à l'équilibre entre les ions dans le complexe activé. En solution aqueuse, pour $r = 2 \text{ \AA}$, l'équation [4] devient

$$[5] \quad \Delta S \sim -10 Z_a Z_b,$$

ce qui est en accord avec les résultats expérimentaux dans ce cas-ci: $Z_a = -4$, $Z_b = 1$. Il pourrait être intéressant de noter que la formation de l'acide ATPH^{-3} à partir de ATP^{-4} et de H^+ s'accompagne d'un changement d'entropie d'environ 32 à 34 unités d'entropie (10, 11). Bien que les deux processus soient probablement différents, on peut s'attendre à ce que les mêmes effets électrostatiques entrent en jeu. Dans les deux cas, par exemple, on a neutralisation de charges, ce qui amènerait une augmentation considérable de l'entropie, par libération des molécules de l'eau d'hydratation des ions (8).

Cette observation suggère que la neutralisation des charges soit le facteur le plus important qui contribue à l'entropie d'activation dans le cas de réactions entre ions en solution aqueuse. Une conclusion semblable peut se tirer d'autres données sur les réactions ioniques (référence 5, p. 435).

L'énergie d'activation (29.2 kcalories/mole) peut être comparée à deux types de données: les données sur l'équilibre d'association, où le changement d'enthalpie est à peu près nul, ou légèrement positif, et les données sur l'hydrolyse en milieu acide (pH 1.3) où l'enthalpie d'activation est 20.7 kcalories/mole (4). La stabilisation de la molécule d'ATP par résonnance (7) pourrait peut-être expliquer la différence de 8 kcalories/mole entre l'énergie d'activation obtenue à pH 1.3 et celle obtenue à des pH supérieurs à 8. On note qu'en présence de soude 0.01 N , l'énergie d'activation est la même qu'à pH 8.8. La comparaison des formules de l'ATP à pH 8 et à pH 1 peut être intéressante de ce point de vue.



L'hydrolyse de l'ion (b) dont la charge négative n'est probablement pas sur le phosphate terminal (11), pourrait peut-être n'être qu'une réaction entre une molécule sans charge électrique et un ion ce qui expliquerait peut-être que l'entropie d'activation est négative: -17 u.e. (4).

D'autre part, il semble que l'ion (a) sera stabilisé de façon considérable par résonnance, par rapport à l'ion (b). Cependant la répulsion entre charges électriques aurait

normalement une tendance à rendre l'ion instable et à diminuer la valeur de l'énergie de la liaison terminale P—O—P. L'hydrolyse de l'ADP pourrait nous fournir des données additionnelles sur ce sujet.

SUMMARY

Data are reported on the kinetics of the alkaline hydrolysis of adenosine triphosphate. Between pH 8 and pH 9, the reaction rate can be written as

$$-d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+],$$

and k can be expressed as

$$k = (eRT/Nh)\exp(39.2/R - 29200/RT).$$

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VOLTAIC CELLS IN FUSED SALTS

PART II. THE SYSTEMS: (a) SILVER - SILVER CHLORIDE, LEAD - LEAD CHLORIDE; (b) SILVER - SILVER CHLORIDE, ZINC - ZINC CHLORIDE; AND (c) SILVER - SILVER CHLORIDE, NICKEL - NICKELOUS CHLORIDE¹

S. N. FLENGAS² AND T. R. INGRAHAM³

ABSTRACT

Using a reversible silver-silver chloride reference electrode, described in the first paper of this series, standard electrode potentials have been established for the systems lead-lead chloride, zinc-zinc chloride, and nickel-nickelous chloride, in melts containing equimolar quantities of KCl and NaCl. Deviations from ideality were observed, and these were attributed to the formation of complexes. Dissociation constants for the complexes were calculated. The effect of temperature on the electromotive forces of the voltaic cells was also measured, and the heats of the cell reactions were calculated from the data.

INTRODUCTION

Part I of this series (1) described the development and use of a reversible silver-silver chloride electrode for measuring the electromotive forces of a cobalt-silver voltaic cell in chloride melts at high temperatures.

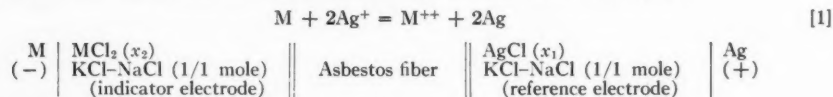
In this second paper of the series, experiments will be described in which the reversible silver-silver chloride electrode was combined with half-cells containing respectively lead-lead chloride, zinc-zinc chloride, and nickel-nickelous chloride electrodes. An equimolar mixture of molten potassium and sodium chlorides was used as the common solvent.

These results are an additional contribution to the program in these laboratories of establishing an electromotive series of metals in molten salts for different temperatures.

EXPERIMENTAL

The apparatus and technique used to study the lead, zinc, and nickel systems were essentially the same as those developed for studying the cobalt system, with the exception that the indicator electrodes for lead and zinc were redesigned to permit the use of the molten metals as electrodes. The simple electrode design is shown in Fig. 1, from which it will be evident that electrical connection with the pool of molten metal within the indicator electrode was made by a tungsten wire dipped into the metal. All of the metals used in these experiments were of high purity, e.g. 99.99%, and argon was used as an inert gas cover on the cells. As previously described (1), the argon flow was discontinued during the actual electromotive force measurements to permit steady values to be obtained.

The cell reaction for voltaic cells of the following type, in ideal solution, is:



where M is, respectively, lead, zinc, or nickel.

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Contribution from the Department of Mines and Technical Surveys, Ottawa. Published with the permission of the Director, Mines Branch, Ottawa.

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The electromotive force of the experimental voltaic cell should obey the Nernst equation expressed as:

$$E_{\text{cell}} = (E_{\text{M}}^{\circ} - E_{\text{Ag}}^{\circ}) - (2.303RT/2\mathcal{F})\log(x_2/x_1^2), \quad [2]$$

where E_{M}° and E_{Ag}° are respectively the standard electrode potentials of the half-cells $\text{MCl} \mid \text{M}_2$ and $\text{Ag} \mid \text{AgCl}$ under the conditions of the experiments, and x_1 and x_2

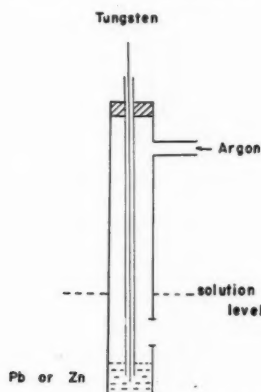


FIG. 1. All silica indicator electrode.

are respectively the mole fractions of AgCl and MCl_2 in the alkali chloride melt solvent.

The electromotive forces of these cells were measured as a function of both the concentration of the indicator metal ion and the temperature of the cell.

RESULTS

The results of the experiments in which the concentration of the metal ion was varied at constant temperature are shown in Table I.

From equation [2] it follows that the relationship between E_{cell} and $\log(x_2/x_1^2)$ should be linear, and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{\text{cell}} = E_{\text{M}}^{\circ} - E_{\text{Ag}}^{\circ}.$$

When the electromotive forces of the cells were plotted against $\log(x_2/x_1^2)$ as calculated from the experimental data given in Table I, the results were represented by straight lines, in agreement with the theory, as shown in Fig. 2. The slopes of the experimental straight lines agree well with the theoretical values calculated from equation [2], for a two-electron electrode process. The results of these calculations are given in Table II. Also included in the table are values for the standard potentials of the cells derived graphically from the curves in Fig. 2, and theoretical standard potentials calculated from data given by Hamer, Malmberg, and Rubin (2).

In the above table it is of theoretical interest to compare the experimentally obtained standard potentials of the voltaic cells with the theoretical values calculated from purely thermodynamic data. The differences have been attributed to the formation of complexes between the metal chlorides and the alkali chloride melt solvent. The dissociation constants, K_d , of these complexes have been calculated from the differences between the

TABLE I
ELECTROMOTIVE FORCES OF VOLTAIC CELLS AS A FUNCTION OF THE METAL ION
CONCENTRATION IN THE INDICATOR ELECTRODE

(a)		Pb (-)	PbCl ₂ in 1/1 mole KCl-NaCl		AgCl in 1/1 mole KCl-NaCl		Ag (+)
Mole fraction of AgCl (<i>x</i> ₁)			Mole fraction of PbCl ₂ (<i>x</i> ₂)		<i>t</i> , ° C.		<i>E</i> _{cell} (volts)
7.219×10 ⁻²			3.254×10 ⁻⁴		682		0.4638
"			9.808×10 ⁻⁴		"		0.4318
"			1.827×10 ⁻³		"		0.4107
"			3.818×10 ⁻³		"		0.3822
"			8.116×10 ⁻³		"		0.3533
"			6.276×10 ⁻²		"		0.2775
(b)		Zn (-)	ZnCl ₂ in 1/1 mole KCl-NaCl		AgCl in 1/1 mole KCl-NaCl		Ag (+)
Mole fraction AgCl (<i>x</i> ₁)			Mole fraction of ZnCl ₂ (<i>x</i> ₂)		<i>t</i> , ° C.		<i>E</i> _{cell} (volts)
7.201×10 ⁻²			2.219×10 ⁻³		684		0.876
"			6.438×10 ⁻³		"		0.834
"			1.376×10 ⁻²		"		0.801
"			2.496×10 ⁻²		"		0.772
"			5.529×10 ⁻²		"		0.738
"			7.710×10 ⁻²		"		0.734
(c)		Ni (-)	NiCl ₂ in 1/1 mole KCl-NaCl		AgCl in 1/1 mole KCl-NaCl		Ag (+)
Mole fraction of AgCl (<i>x</i> ₁)			Mole fraction of NiCl ₂ (<i>x</i> ₂)		<i>t</i> , ° C.		<i>E</i> _{cell} (volts)
6.235×10 ⁻²			5.938×10 ⁻⁴		705		0.2293
"			2.622×10 ⁻³		"		0.1570
"			9.069×10 ⁻³		"		0.1003
"			1.392×10 ⁻²		"		0.0785
"			2.454×10 ⁻²		"		0.0501
"			4.612×10 ⁻²		"		0.0193
"			6.236×10 ⁻²		"		0.0070

TABLE II
COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS FOR THE Pb, Zn, AND Ni
ELECTRODE SYSTEMS

Cell reaction	t , ° C.	$E^\circ_{\text{M}} - E^\circ_{\text{Ag}}$ (volts)		Slope	
		Exptl.	Calc.	Exptl.	Calc.
Pb + 2Ag ⁺ = Pb ⁺⁺ + 2Ag	682	0.370	0.320	0.093	0.094
Zn + 2Ag ⁺ = Zn ⁺⁺ + 2Ag	684	0.840	0.665	0.093	0.095
Ni + 2Ag ⁺ = Ni ⁺⁺ + 2Ag	705	0.135	0.087	0.097	0.097

experimental and theoretical standard potentials, using the method previously described (1). The calculated values are:

$$K_a (\text{Pb complex}) = 2.9 \times 10^{-1},$$

$$K_a (\text{Zn complex}) = 1.5 \times 10^{-2},$$

$$K_a (\text{Ni complex}) = 3.0 \times 10^{-1}.$$

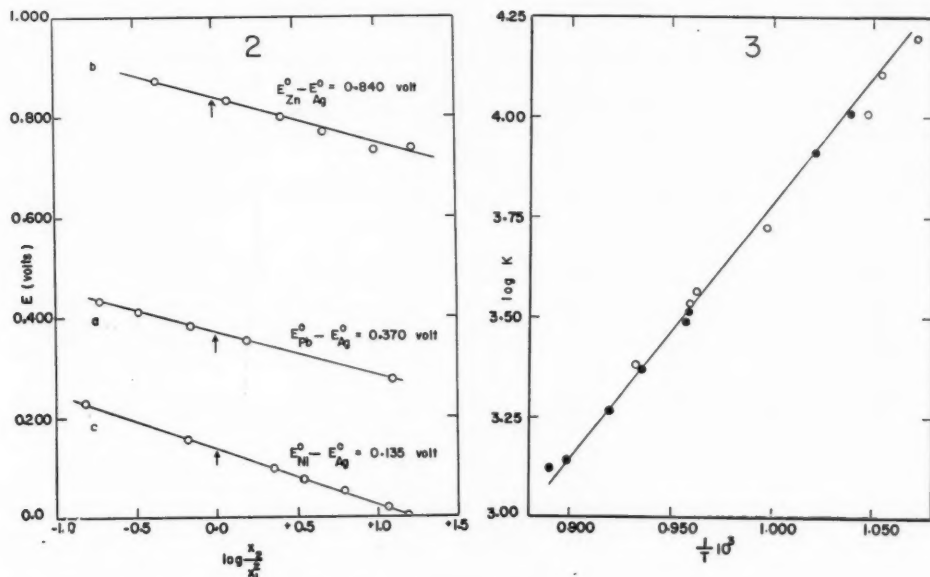


FIG. 2. Electromotive forces of the cells:

$$M \mid MCl_2(x_2) \parallel KCl-NaCl(1/1 \text{ mole}) \parallel AgCl(x_1) \mid Ag$$
 as a function of $\log(x_2/x_1)$ at a constant temperature. M is respectively (a) lead, (b) zinc, and (c) nickel.

FIG. 3. The variation of $\log K$ with the reciprocal of absolute temperature for the system:

$$Pb \mid PbCl_2(x_2 = 6.276 \times 10^{-2}) \parallel AgCl(x_1 = 7.219 \times 10^{-2}) \mid Ag$$

$$\mid KCl-NaCl(1/1 \text{ mole}) \parallel KCl-NaCl(1/1 \text{ mole}) \mid Ag$$
 ○ with increasing temperature, ● with decreasing temperature.

The magnitude of the constants indicates that the complexes formed by lead chloride and nickel chloride are very weak, and that the complex formed by zinc chloride is fairly stable.

The effect of temperature change on the electromotive force of the voltaic cells was also investigated. The results of these experiments, for a temperature range between 650° and 850° C., are given in Table III. Also included in Table III are values for the standard potentials calculated from the data using equation [2].

From the standard potentials given in Table III, using the well-known equations:

$$\Delta F^\circ = -nE^\circ \mathcal{F}, \quad [3]$$

$$\Delta F^\circ = -2.303RT \log K, \quad [4]$$

it was possible to calculate, for various temperatures, the effective equilibrium constants for the cell reactions given in Table II. These equilibrium constants are understood to include any effects due to the presence of the solvent.

The results of these calculations are shown in Figs. 3, 4, and 5, where $\log K$ was plotted against the reciprocal of the absolute temperature. The curves are linear over the temperature range investigated. For each curve, the best straight line through the experimental points was calculated by applying the least squares method. The average deviations of the experimental $\log K$ values were of the order of ± 0.020 .

The heat of reaction (ΔH_r), in cells of this type, is the difference between the heats of formation of the respective chlorides in the melt (ΔH_f), i.e.

$$\Delta H_r = \Delta H_{f(MCl_2 \text{ in } KCl-NaCl)} - 2\Delta H_{f(AgCl \text{ in } KCl-NaCl)}.$$

TABLE III
EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELLS

M | MCl₂ in KCl-NaCl || AgCl in KCl-NaCl | Ag
where M is, respectively, lead, zinc, or nickel

Pb-Ag voltaic cell*			Zn-Ag voltaic cell†			Ni-Ag voltaic cell‡		
T, ° K.	E _{cell} (volts)	E° _{Pb} - E° _{Ag} (volts)	T, ° K.	E _{cell} (volts)	E° _{Zn} - E° _{Ag} (volts)	T, ° K.	E _{cell} (volts)	E° _{Ni} - E° _{Ag} (volts)
On heating								
933	0.2888	0.3890	940	0.7427	0.8490			
949	0.2858	0.3876	961	0.7394	0.8481	1013	-0.0200	0.1039
955	0.2775	0.3799	967	0.7378	0.8472	1021	-0.0237	0.1010
1003	0.2625	0.3700	989	0.7282	0.8462	1043	-0.0295	0.0979
1040	0.2560	0.3673	1001	0.7248	0.8378	1111	-0.0497	0.0859
1043	0.2543	0.3659	1015	0.7173	0.8319			
1073	0.2448	0.3597	1018	0.7155	0.8305			
			1033	0.7095	0.8261			
			1047	0.7036	0.8217			
			1058	0.6982	0.8176			
			1068	0.6918	0.8125			
			1088	0.6871	0.8098			
			1098	0.6838	0.8076			
			1103	0.6803	0.8046			
On cooling								
1123	0.2221	0.3470	1109	0.6791	0.8041	1103	-0.0448	0.0900
1113	0.2271	0.3459	1098	0.6848	0.8086	1083	-0.0402	0.0923
1088	0.2351	0.3516	1083	0.6920	0.8140	1063	-0.0340	0.0960
1069	0.2427	0.3570	1073	0.6962	0.8172	1037	-0.0292	0.0976
1045	0.2487	0.3616	1048	0.7071	0.8254			
1043	0.2517	0.3633	1028	0.7152	0.8312	988	-0.0105	0.1104
979	0.2747	0.3796	1009	0.7220	0.8360	938	-0.0082	0.1229
963	0.2805	0.3837	993	0.7294	0.8416			
			968	0.7419	0.8513			
			963	0.7446	0.8529			

*The mole fractions of AgCl and PbCl₂ were respectively 7.219×10^{-2} (x_1) and 6.276×10^{-2} (x_2).

†The mole fractions of AgCl and ZnCl₂ were respectively 7.201×10^{-2} (x_1) and 7.150×10^{-2} (x_2).

‡The mole fractions of AgCl and NiCl₂ were respectively 6.234×10^{-2} (x_1) and 6.656×10^{-2} (x_2).

These heats of reaction were calculated from the slopes of the straight lines in Figs. 3, 4, and 5, in accordance with the van't Hoff equation:

$$d \ln K / dT = \Delta H_r / RT^2.$$

The results thus obtained are:

$$\Delta H_r (\text{Pb-Ag}) = -29.0 \pm 1.0 \text{ kcal.},$$

$$\Delta H_r (\text{Zn-Ag}) = -54.4 \pm 1.3 \text{ kcal.},$$

$$\Delta H_r (\text{Ni-Ag}) = -14.0 \pm 1.0 \text{ kcal.}$$

It will be noted that these values include any effects due to the presence of solvent.

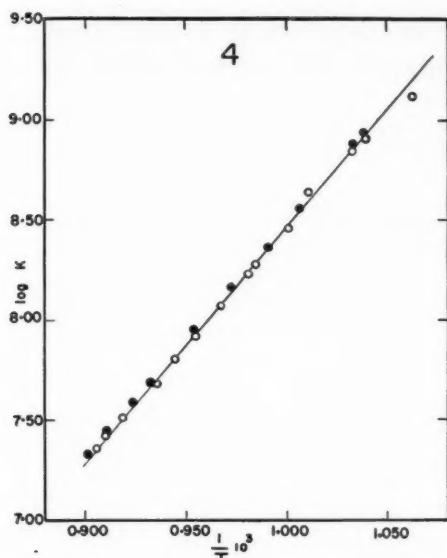
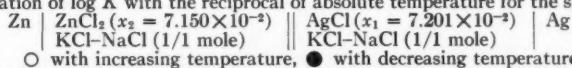


FIG. 4. The variation of $\log K$ with the reciprocal of absolute temperature for the system:



○ with increasing temperature, ● with decreasing temperature.

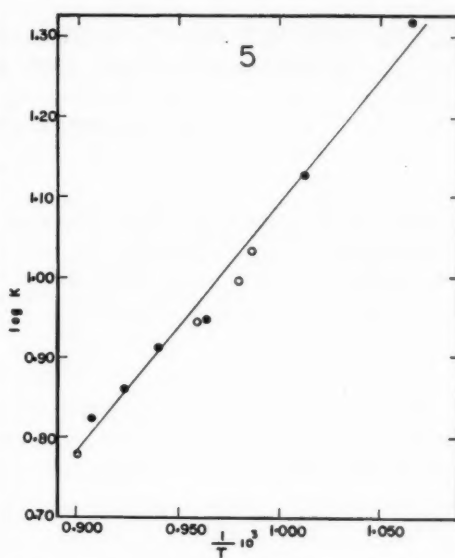
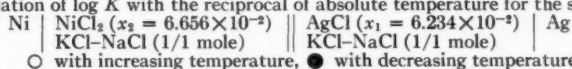


FIG. 5. The variation of $\log K$ with the reciprocal of absolute temperature for the system:



○ with increasing temperature, ● with decreasing temperature.

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PREPARATION OF GUANIDINE FROM AMMONIUM THIOCYANATE, SULPHUR DIOXIDE, AND AMMONIA UNDER PRESSURE¹

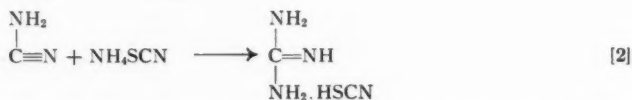
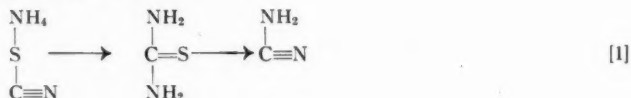
JEAN L. BOIVIN AND MEUDE TREMBLAY

ABSTRACT

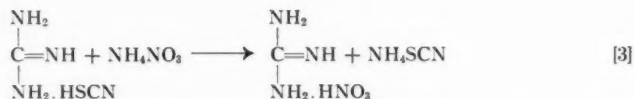
Nearly quantitative yields of guanidine have been obtained by heating a mixture of ammonium thiocyanate, sulphur dioxide, and ammonia under moderate pressure. Guanidine is present chiefly as the sulphamate. When a molar ratio of ammonium thiocyanate, sulphur dioxide, and ammonia of 1:3:7 respectively was used, approximately one mole of guanidine sulphamate was produced together with half a mole of ammonium sulphate and more than two moles of elemental sulphur. The reaction products are in the molten state at the synthesis temperature, and with a suitable reactor capable of withstanding corrosion, the reaction has possibilities as a continuous process.

INTRODUCTION

Prior to the large scale production of calcium cyanamide, guanidine was made commercially from ammonium thiocyanate. By heating this material at a temperature of about 200–250° C. guanidine thiocyanate is obtained.



From the above equations it can be deduced that yields could not be higher than 50%. To render this synthesis attractive, there is need for an efficient recovery of thiocyanate ion in a form suitable for recycling. By double decomposition of guanidine thiocyanate with ammonium nitrate, sparingly soluble guanidine nitrate and ammonium thiocyanate are formed.



The recovery of ammonium thiocyanate, however, is not quantitative and the reaction product is always contaminated with nitrate ion, which destroys a part of the ammonium thiocyanate in subsequent runs. Moreover, the guanidine nitrate is not free of sulphur compounds, and a method of producing guanidine in a more suitable form, making use of the same starting material, is desirable.

Several modifications of the fundamental reaction have been investigated. Ammonium thiocyanate has been reacted with ammonium nitrate producing guanidine nitrate and sulphur, the reaction proceeding as a result of the oxidation of hydrogen sulphide by ammonium nitrate. This process is hazardous, and several explosions have occurred as a result of violent oxidation of hydrogen sulphide by ammonium nitrate.

¹Manuscript received July 16, 1957.

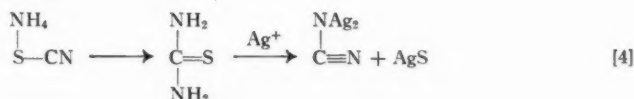
Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec. Issued as C.A.R.D.E. Technical Memo No. 59/51 (December 1951).

Recently Hill (2) obtained a patent on a process in which ammonium thiocyanate is heated with ammonium sulphamate. It is claimed that a yield of 75% is obtained and the product is free of hydrogen sulphide. This latter claim is subject to doubt.

Following the successful use of sulphur dioxide in the conversion of urea into high yields of guanidine (1), it was thought that the same reagent would be successful in the conversion of ammonium thiocyanate into guanidine.

Mechanism of the Reaction

It has long been known that when it is heated, ammonium thiocyanate is transformed into its isomeric compound, thiourea, which on being heated above its melting point produces guanidine thiocyanate. Moreover, the formation of cyanamide has been demonstrated by treating an aqueous solution of thiourea with silver ions, silver cyanamide and silver sulphide being formed.



Therefore the over-all equation is

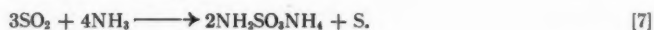


In the presence of sulphur dioxide hydrogen sulphide will be transformed into sulphur and water.

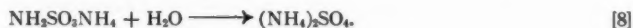


The presence of water decreases the efficiency of the synthesis of guanidine.

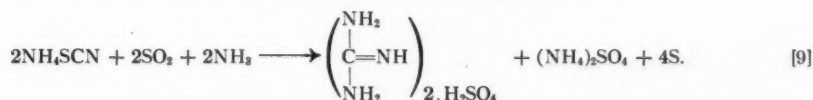
It has been shown (1) that under suitable conditions sulphur dioxide and ammonia react according to the following over-all equation:



The ammonium sulphamate formed would react with the water produced by the oxidation of hydrogen sulphide according to the following equation:



Therefore the over-all equation representing the reaction involved is



GENERAL PROCEDURE

Sulphur dioxide, ammonium thiocyanate, and ammonia were introduced into a 100-ml. autoclave. The mixture was heated at a desired temperature for a period of time under pressure. When reaction was completed, the products were leached with water, the mixture filtered free of sulphur, and the filtrate used for analysis and subsequent treatment.

Effect of Temperature

Mixtures of ammonium thiocyanate, sulphur dioxide, and ammonia were heated at

different temperatures for $\frac{1}{2}$ hour at a gauge pressure of 500 p.s.i. Results shown in Table I indicate that a yield of 80% or better can be achieved over a wide range of temperature (225° to 275° C.). At temperatures above 275° C., melamine starts to be produced, thus decreasing the yield of guanidine.

TABLE I
EFFECT OF TEMPERATURE
Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole; ammonia: 0.9 mole; time: 30 min.; pressure: 500 p.s.i.g.*

Run No.	Temperature, °C.	Guanidine,† % yield
670	175	24
671	200	32
672	225	78
673	250	83
674	275	83
675	300	72

* Vented to this pressure.

† All yields are based on ammonium thiocyanate.

Effect of Ammonium Thiocyanate

Using a constant amount of sulphur dioxide and keeping constant conditions of temperature, pressure, and time of heating, concentration of ammonium thiocyanate was varied. It was observed that with 0.05 mole of starting materials, maximum yield is obtained (Table II). This result is equivalent to the reaction of ammonium thiocyanate in an excess of sulphur dioxide.

TABLE II
EFFECT OF AMMONIUM THIOCYANATE
Sulphur dioxide: 0.3 mole; ammonia: 0.9 mole; temp.: 275° C.; time: 30 min.; pressure: 500 p.s.i.g.

Run No.	Ammonium thiocyanate, mole	Guanidine, % yield
683	0.05	89
684	0.10	83
685	0.15	60
686	0.20	43

Effect of Sulphur Dioxide

The most significant variable is the amount of sulphur dioxide. In Table III it is observed that yields of guanidine varied with the amounts of sulphur dioxide employed, the yields being nearly quantitative when the molar ratio of ammonium thiocyanate to sulphur dioxide is 1:4.

Effect of Ammonia

As anticipated, ammonia is important in this synthesis. It is noted that the absence of ammonia gives low yields of guanidine under the reaction conditions (Table IV). However, ammonia pressure is not absolutely necessary and a satisfactory yield of guanidine can be obtained under a sulphur dioxide pressure (150 p.s.i.g.), as in Run 691.

TABLE III

EFFECT OF SULPHUR DIOXIDE

Ammonium thiocyanate: 0.1 mole; ammonia: 0.9 mole;
temp.: 275° C.; time: 30 min.; pressure: 500 p.s.i.g.

Run No.	Sulphur dioxide, mole	Guanidine, % yield
687A	0.0	30
687	0.1	41
688	0.2	65
689	0.3	83
689A	0.4	83

TABLE IV

EFFECT OF AMMONIA

Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole; temp.:
275° C.; time: 30 min.

Run No.	Ammonia, mole	Pressure, p.s.i.g.	Guanidine, % yield
690	0.0	500	24
691	0.3	(sul. diox.) 150	72
692	0.6	(sul. diox.) 300	83
693	0.8	(ammonia) 600	83
		(ammonia)	

Effect of Pressure

Although the guanidine synthesis is generally believed to take place under moderate pressure, in this synthesis an abnormally low pressure is effective. As shown in Table V, a pressure of 50 p.s.i.g. is capable of giving 80% yield or better. A greater pressure (1000–2000 p.s.i.g.) does not improve the yield but tends to give slightly lower values.

TABLE V

EFFECT OF PRESSURE

Ammonium thiocyanate: 0.1 mole; sulphur dioxide:
0.3 mole; ammonia: 0.9 mole; temp.: 275° C.; time:
30 min.

Run No.	Pressure, p.s.i.g.	Guanidine, % yield
701	0	75
701A	50	83
702	100	83
703	200	83
704	300	83
705	500	83
706	1000	78
707	2000	77

Effect of Time

Another important variable is the period of heating. It is anticipated that reaction will occur in a few minutes at high temperature and only after several hours at reduced temperatures. In Table VI it is noted that at 225° C. the yield decreases with time at

a pressure of 500 p.s.i.g. This is also true at temperatures of 250° and 275° C. Since yields decreased with time at a pressure of 500 p.s.i.g., a lower pressure (200 p.s.i.g.) was used. Maximum yield is obtained after 60 minutes of heating at 225° C. At 250° C. the yield increases with time up to 90 minutes of heating when 93% yield is achieved. With a view to operating this reaction continuously, the effect of shorter periods of heating was investigated. For 5 minutes of heating at 225° C. reaction is incomplete and the yield is only 66%. At 250° and 275° C. yields of 86 and 85% respectively were obtained.

TABLE VI
EFFECT OF TIME
Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole;
ammonia: 0.9 mole

Run No.	Temperature, °C.	Time, min.	Pressure, p.s.i.g.	Guanidine, % yield
694	225	30	500	78
695	225	60	500	75
696	225	90	500	75
697	225	120	500	68
680	250	30	500	83
681	250	60	500	83
682	250	90	500	80
705	275	30	500	83
698	275	60	500	83
699	275	90	500	81
700	275	120	500	71
725	250	30	200	84
726	250	60	200	90
727	250	90	200	93
728	250	120	200	90
735	225	5	200	66
736	250	5	200	86
737	275	5	200	85

DISCUSSION OF RESULTS

Formation of Guanidine Sulphamate

When ammonium thiocyanate, sulphur dioxide, and ammonia in a molar ratio of 1:3:7 were heated at 250° for 1 hour under an ammonia pressure of 200 p.s.i.g., guanidine was present as the sulphamate. Therefore this synthesis produces the same products as the preparation of guanidine from urea, sulphur dioxide, and ammonia (1). Practically all guanidine formed was present as the sulphamate, a small amount being in the form of sulphate.

Sulphur Formation

It has been reported (1) that sulphur is produced along with ammonium sulphamate when sulphur dioxide is heated with ammonia (Equation [7]). The amount of sulphur from sulphur dioxide is almost constant at 33%. In the actual synthesis the amount of sulphur isolated was found to be more than twice the quantity predicted in Equation [9]. Therefore a part of the sulphur must come from the synthesis of ammonium sulphamate (Equation [7]) and the remainder from ammonium thiocyanate by a reaction as suggested in Equation [6].

Formation of Ammonium Sulphate

The amount of ammonium sulphate formed (viz., $\frac{1}{2}$ mole for each mole of guanidine

produced) is lower than in the urea-sulphur dioxide-ammonia reaction. Owing to the relatively soluble ammonium sulphate in the reaction products, this makes possible a continuous reaction.

Isolation of Guanidine Nitrate

Guanidine nitrate is easily obtained by treating the sulphur-free reaction products with dilute nitric acid. From preliminary experiments it was observed that guanidine nitrate is readily soluble in ammonium sulphamate solution. Therefore it is essential to complete hydrolysis of any sulphamate in order to obtain a satisfactory recovery.

Conversion to Nitroguanidine

The sulphur-free reaction products were treated with concentrated sulphuric acid at 100° C. and the solution cooled to 40° C. while nitric acid was added. An over-all yield of 80% of picrite was obtained from ammonium thiocyanate. It is anticipated that a higher yield is possible from guanidine nitrate.

CONCLUSION

The reaction of ammonium thiocyanate, sulphur dioxide, and ammonia under moderate pressure gives excellent yields of guanidine. An encouraging feature is that the quantity of ammonium sulphate formed is much lower than in the urea-sulphur dioxide-ammonia reaction (1). The quantity is $\frac{1}{2}$ mole for each mole of guanidine present. Since the reaction products are molten at the operating temperature, the reaction offers considerable promise for development into a continuous process. Unfortunately the reaction is highly corrosive on stainless steel, corrosion increasing with temperature. It is hoped that some suitable metal or alloy can be found to resist corrosion at temperatures around 225° C. It is known that tantalum and titanium would be satisfactory under these conditions, but a less expensive and more readily available metal would be preferable.

EXPERIMENTAL

Procedure for Run 726

Into a glass liner immersed in a dry ice-acetone bath was successively added liquid sulphur dioxide (19.2 g., 0.3 mole), urea (6.0 g., 0.1 mole), and liquid ammonia (15.3 g., 0.9 mole). The cold mixture was introduced into the bomb and heated at 250° C. for 1 hour at a pressure of 200 p.s.i.g., vented to this pressure. The bomb was cooled, opened, and the contents of the glass liner leached with hot water. Sulphur (7.5 g.) was filtered off and the filtrate was used for analytical purposes. Analytical results: guanidine, 0.09 mole; sulphur, 0.234 mole; ammonium sulphate, 0.0421 mole. According to Equation [9], molar quantities of guanidine should be 0.1; sulphur 0.2; and ammonium sulphate 0.05.

Identification of Guanidine Sulphamate

A run similar to No. 726 was made from 0.1 mole of ammonium thiocyanate evaporated to dryness. The residue was extracted with liquid ammonia and the solution allowed to evaporate. The crystalline product was dissolved in a large volume of ethanol and allowed to crystallize: 125-126° C. A mixed melting point determination with guanidine sulphamate was not depressed. The material insoluble in liquid ammonia was chiefly ammonium sulphate with traces of guanidine sulphate.

Guanidine Nitrate

A run similar to No. 726 was made from 0.1 mole of ammonium thiocyanate. Sulphur

was filtered off and the filtrate boiled 1 hour with nitric acid (70%, 10 g.). The solution was evaporated to 50 ml. and allowed to stand overnight at 0° C. The crystals were filtered and washed with a saturated solution of guanidine nitrate at 0° C. The product weighed 10.0 g. (82% from ammonium thiocyanate) and melted at 204–206° C. The nitration of guanidine nitrate in 98% sulphuric acid (30 g.) yielded 7.5 g. of nitroguanidine (72% from ammonium thiocyanate).

Nitroguanidine from Crude Product

Crude product from a run similar to 726 was freed of sulphur by filtration. The filtrate was evaporated to dryness and the residue treated with 98% sulphuric acid (65 g.). The mixture was heated at 100° C. for an hour and cooled to 38° C. Nitric acid (96%, 6.3 g.) was added slowly at a temperature of 38–40° C. and stirred at this temperature for 20 minutes. Nitroguanidine was isolated in the usual manner. Yield, 8.2 g. (80% from ammonium thiocyanate).

REFERENCES

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PHOTO-INITIATED FREE RADICAL POLYMERIZATION OF METHYL ACRYLATE IN AQUEOUS SOLUTION¹

C. CHAITANYAN MENON AND M. SANTAPPA

ABSTRACT

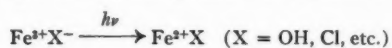
Photo-initiated free radical polymerization of methyl acrylate in aqueous solution is described. Using mainly light of wavelength 3650 Å and the ion pairs $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ as photosensitizers the kinetics of polymerization were investigated by studying the effect of the variation of (i) intensity of light, (ii) concentration of monomer, (iii) fraction of light absorbed by the ion pair, and (iv) ferrous ion accumulating in, or initially added to, the system on (a) molecular weight of polymer, (b) the rate of disappearance of monomer, and (c) the rate of production of ferrous ion. The results have been analyzed in the light of a reaction scheme involving (1) a primary photochemical process and a dark back reaction, (2) initiation of polymerization by the primary product Fe^{2+}OH or Fe^{2+}Cl , (3) dissociation of the primary product, (4) a secondary dark back reaction, (5) initiation by a free radical, (6) propagation, and (7) termination. Examination of the experimental results in the light of the reaction scheme indicated that the initiation of polymerization was due to OH or Cl free radicals formed by the dissociation of the primary product and that termination occurred by combination of growing polymer chains. Some expressions involving specific rate constants have been evaluated.

INTRODUCTION

Baxendale, Evans, and Park (1) have shown that the OH radicals produced in the reaction between hydrogen peroxide and ferrous ion initiate polymerization of vinyl monomers in aqueous solution. Rabinowitch and Stockmayer (2) have interpreted the spectra of ferric association complexes as "electron transfer spectra". The presence of "association complexes" or "ion-pair complexes" was also inferred by Fromherz and Lih (3) in their studies of lead halide solutions and by Davies and Wyatt (4) in investigations of numerous other salt solutions. Evans and Uri (5) have shown that atoms and free radicals produced by irradiation of ferric ion-pair complexes lead to polymerization of vinyl compounds in aqueous solution. These workers and Santappa (6, 7, 8, 9) have made systematic investigations of the polymerization of acrylonitrile and methyl methacrylate by the ion pairs $\text{Fe}^{3+}\text{OH}^-$, $\text{Fe}^{3+}\text{Cl}^-$, and $\text{Fe}^{3+}\text{N}_3^-$. Studies of the polymerization of methyl acrylate monomer even under thermal conditions have been very scanty because of the tough and elastic nature of the polymer formed under conditions of "auto-acceleration". Matheson and co-workers (10) have evaluated the specific rate constants for initiation, growth, and termination in the polymerization of this monomer. In this paper we wish to present in detail work on the polymerization of methyl acrylate by the ion-pair complexes $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$.

Light Absorption and Electron Transfer

It is assumed that the light absorption process is connected with an electron transfer:



Dissociation of the complex Fe^{2+}X into Fe^{2+} and X is expected (6) on energetic grounds. Radicals, X, thus produced lead to subsequent reactions like polymerization of vinyl compounds.

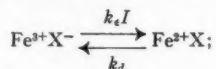
¹Manuscript received January 21, 1957.

Contribution from the Physical Chemistry Laboratory, University of Madras, Guindy, Madras 25, India. From a M.Sc. thesis presented by C. Chaitanyan Menon to the University of Madras. Presented in part to the Seventh Canadian High Polymer Forum, Sarnia, Ontario, Canada, November 8-9, 1956.

The Reaction Scheme

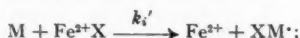
The following scheme includes those reactions which are likely to occur:

- (1) Light absorption and primary dark back reaction:



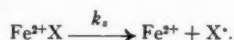
k_a is the fraction of light absorbed by Fe^{3+}X^- and I is the light intensity.

- (2) Initiation of polymerization by primary product $\text{Fe}^{2+}\text{X}^{\cdot}$:

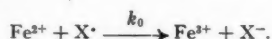


M represents vinyl monomer.

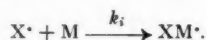
- (3) Separation of primary product:



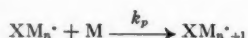
- (4) Secondary dark back reaction:



- (5) Initiation of polymerization by free radicals X $^{\cdot}$:



- (6) Propagation of polymerization:



- (7) Termination of polymerization with rate constant k_t .

EXPERIMENTAL

A 250 watt high pressure mercury vapor lamp (Gallenkamp, *dp* 7094) provided a bright source of light with the principal wavelengths 3650, 4046, 4358 Å, etc. The maximum arc brightness was 2×10^4 candles/cm 2 . The lamp was a silica sphere mounted inside a metal shield 100 by 65 by 55 mm. fitted with a circular glass window. The lamp was stabilized by choke Z,1875, Gallenkamp *dp* 7094/1. For the 3130 Å line the light source was a 250 watt high pressure mercury vapor lamp supplied by B.T.H., U.K. The light from the lamps passed through a quartz condenser lens and the resulting parallel beam was passed through a series of filters to isolate the monochromatic lines. The principal line used was 3650 Å; lines at 3130, 4050, and 4350 Å were also used to some extent. The respective filters for the isolation of these lines are given by Bowen (11). The light beam consisting of the monochromatic line passed through an adjustable diaphragm into a thermostat fitted with quartz windows and filled with distilled water. At the center of the thermostat was mounted the cylindrical reaction cell with flat quartz plates at both ends and two outlet tubes provided with B 14 cones at the top. The diameter of the cell was 50 mm. and the length in the direction of the optical beam is 46 mm. All experiments were done at 30° C. $\pm 0.1^\circ$, and the duration of irradiation was restricted to 1 hour. With $\text{Fe}^{3+}\text{Cl}^-$ initiator all the experiments were done at pH 1 but with $\text{Fe}^{3+}\text{OH}^-$ initiator most experiments were done at pH 2.

The lamp output was determined by chemical actinometry using uranyl oxalate (12). The light intensities used in our experiments range from 5×10^{-5} to 6×10^{-4} $Nh\nu$ /hour.

The chemicals used were mostly B.D.H. Analar or Merck pure products. Methyl acrylate supplied by Rohm and Haas was repeatedly distilled in an atmosphere of nitrogen and preserved in a refrigerator. Ferric nitrate and ferric perchlorate (10^{-3} to 10^{-5} *M*) were used as sources of ferric ions whose concentration was determined by the standard procedure with Zimmerman-Reinhardt reagent. The concentration of ferrous ions (10^{-4} to 10^{-7} *M*) was determined colorimetrically with ortho phenanthroline as the coloring reagent. Purity of methyl acrylate was determined by the usual bromine addition method. The concentration of the monomer methyl acrylate used was 0.28 *M* for most of the experiments. The rate of disappearance of monomer was followed by weighing the amount of dried polymer.

The experimental conditions for the work closely follow those mentioned by Evans, Santappa, and Uri (6). The system monomer-initiator in aqueous medium was taken in the reaction cell and deaerated by passing oxygen free nitrogen for about one-half hour. The cell was then introduced into the thermostat kept at $30^{\circ}\text{C} \pm 0.1^{\circ}$ and irradiated for about one hour. Turbidity occurred almost instantaneously when the cell was in the path of the light beam indicating the absence of any induction period. Polymer continuously precipitated. At the end of 1 hour, polymer was filtered off and the concentration of ferrous ions in the filtrate was determined colorimetrically.

Purification of polymethyl acrylate was effected by a solution of the polymer in a 1:1 volume mixture of acetone and chloroform, reprecipitation by addition of methanol, followed by drying at 60°C . to constant weight. Molecular weight, *M*, of polymethyl acrylate was determined by measuring the intrinsic viscosity, $[\eta]$, of the polymer in benzene solution and applying the relationship (13):

$$[\eta] = 1.282 \times 10^{-4} M^{0.7145}.$$

RESULTS

(a) Fraction of Light Absorbed, k_a

It has been shown previously (7, 8, 9) that in ferric perchlorate solutions the ion pair $\text{Fe}^{3+}\text{OH}^-$ is the active species, the concentration of the species varying with pH. In the presence of chloride ions the species $\text{Fe}^{3+}\text{Cl}^-$ is also formed. When the system ferric ion pair-methyl acrylate in aqueous solution is irradiated there is a partial reduction of ferric ions to ferrous ions and polymerization of the monomer. Fig. 1 shows the dependence of the rate of formation of ferrous ion using the 3650 \AA line at various fractions of light absorption, k_a , arising from variations in the concentrations of $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$. Changes in the concentration of $\text{Fe}^{3+}\text{OH}^-$ were effected by changing the pH, and changes in the $\text{Fe}^{3+}\text{Cl}^-$ concentration were achieved by changing the ferric ion concentration of the system. It was further found that the rate of disappearance of monomer was a linear function of $k_a^{1/2}$ with $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ as initiators (Fig. 2). The chain length of polymethyl acrylate, produced by $\text{Fe}^{3+}\text{OH}^-$ initiator, was a linear function of $k_a^{-1/2}$ as seen in Fig. 3.

(b) Light Intensity, *I*

Fig. 4 shows the variation of the rate of formation of ferrous ion with light intensity for $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators. It is observed that the relationship deviates from linearity at the high light intensities used in these experiments. A steady state kinetic analysis of the reaction scheme suggested above indicates that the deviations from linearity can be attributed to the condition $k_d[M] \gg k_0[\text{Fe}^{2+}]$ at high light intensities. Fig. 5 shows that the expected linearity between the rate of production of ferrous ion

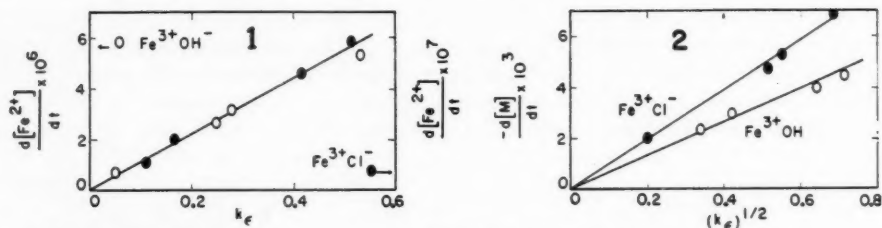


FIG. 1. Rate of production of ferrous ion as a function of fraction of light absorbed.
 FIG. 2. Rate of disappearance of methyl acrylate as a function of fraction of light absorbed.

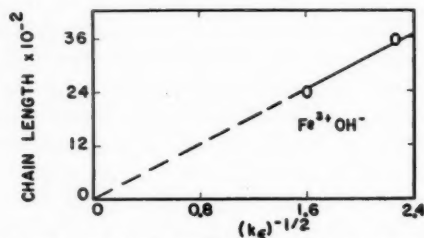


FIG. 3. Chain length of polymethyl acrylate as a function of fraction of light absorbed.

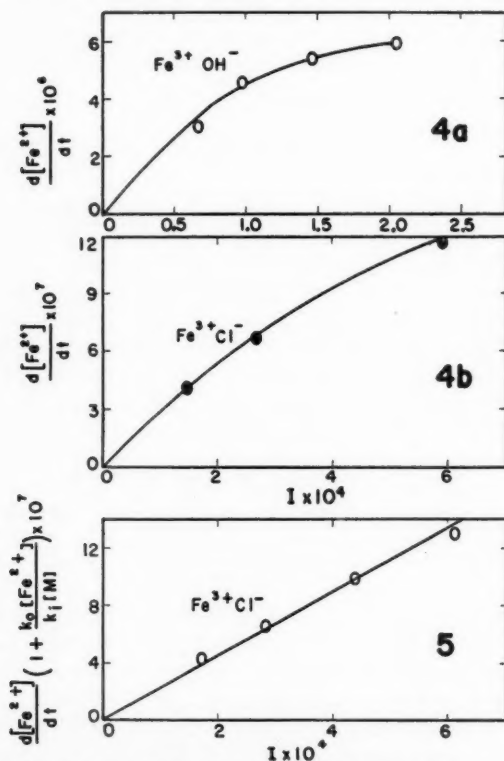


FIG. 4. Rate of formation of ferrous ion as a function of light intensity.
 FIG. 5. Rate of formation of ferrous ion, corrected for secondary dark back reaction, as a function of light intensity.

DETAILS OF EXPERIMENTAL CONDITIONS

For all experiments: wavelength = 3650 Å; temperature = 30° C.; time of experiment = 1 hour

	Figs. 1-3		Figs. 4-7		Figs. 8-10		Fig. 11		Fig. 12	
Fe³⁺OH⁻ initiator										
Monomer	Methyl acrylate		Methyl acrylate		Methyl acrylate		Acrylonitrile		Methyl methacrylate	
Intensity, <i>Nhν</i> /hr.	5.4 × 10 ⁻⁴		0.52 × 10 ⁻⁴ to 2.1 × 10 ⁻⁴		6.1 × 10 ⁻⁴		5.95 × 10 ⁻⁵		5.9 × 10 ⁻⁵	
[Monomer], <i>M</i>	0.283		0.226		0.17 to 0.396		0.3 to 0.75		0.07	
[Fe ³⁺], <i>M</i>	5 × 10 ⁻⁴		1 × 10 ⁻³		1 × 10 ⁻⁴		1 × 10 ⁻³		1 × 10 ⁻³	
pH	1 to 2		2		2		1		1	
									Mean [Fe ³⁺] 0.85 × 10 ⁻⁵ to 3.5 × 10 ⁻⁵ <i>M</i>	
Fe³⁺Cl⁻ initiator										
Monomer	Methyl acrylate		Methyl acrylate		2.3 × 10 ⁻⁴				Methyl acrylate	
Intensity, <i>Nhν</i> /hr.	4.2 × 10 ⁻⁴		1.5 × 10 ⁻⁴ to 6.1 × 10 ⁻⁴		0.17 to 0.396				2.01 × 10 ⁻⁴	
[Monomer], <i>M</i>	0.283		0.283		2 × 10 ⁻³				0.226	
[Fe ³⁺], <i>M</i>	2 × 10 ⁻⁴ to 8 × 10 ⁻⁴		6 × 10 ⁻⁵		0.05				1 × 10 ⁻³	
[Cl ⁻], <i>N</i>	0.05		1		1				0.05	
pH	1		1						1	
									Mean [Fe ³⁺] 2.8 × 10 ⁻⁵ to 8.9 × 10 ⁻⁵ <i>M</i>	

and light intensity is obtained when account is taken of the ferrous ions which are oxidized by chlorine atoms in the secondary dark back reaction. A linear dependence of the rate of disappearance of monomer on the square root of light intensity with $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators could be obtained only at high intensities of light. At low intensities a strong tendency towards non-linearity (Fig. 6) indicated that the scattered light, which

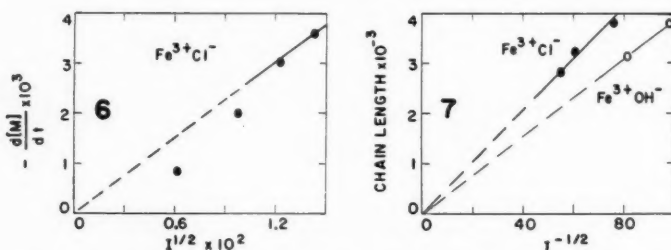


FIG. 6. Rate of disappearance of methyl acrylate as a function of light intensity.
FIG. 7. Chain length of polymethyl acrylate as a function of light intensity.

would have made a considerable contribution to the rate of monomer disappearance, could not be neglected. Further, such behavior was not observed with other monomers previously studied (7, 8, 9) but appeared to be characteristic of polymethyl acrylate. However, linear functions of chain length vs. reciprocal square root of light intensity were obtained with both $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators as illustrated in Fig. 7.

(c) *Monomer Concentration, [M]*

It has been observed (7) with monomers like acrylonitrile and methyl methacrylate that an accurate investigation of the dependence of the rate of production of ferrous ion on monomer concentration was difficult because of interactions of free radicals with impurities (9), especially at low concentrations of monomer. With methyl acrylate and $\text{Fe}^{3+}\text{OH}^-$ initiator there was a regular variation of the rate of production of ferrous ion with monomer concentration whereas with $\text{Fe}^{3+}\text{Cl}^-$ initiator the rate of production of ferrous ion was insensitive to changes in the monomer concentration. Fig. 8 shows the

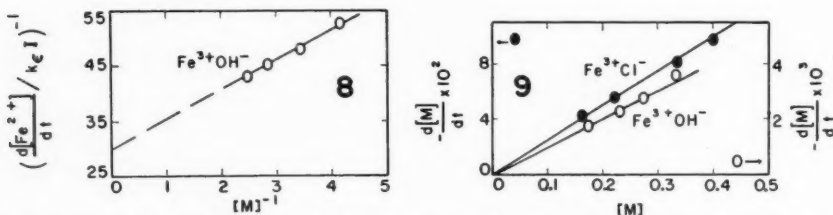


FIG. 8. Quantum yield for production of ferrous ion as a function of concentration of methyl acrylate.
FIG. 9. Rate of disappearance of methyl acrylate as a function of concentration of methyl acrylate.

linear relationship, with $\text{Fe}^{3+}\text{OH}^-$ initiator, between reciprocal quantum yield for ferrous ion production, $1/\gamma$, and reciprocal monomer concentration, $1/[M]$, where

$$\gamma = \frac{d[\text{Fe}^{2+}]/dt}{k_e I}$$

Plots of rate of disappearance of monomer vs. monomer concentration (Fig. 9) and of

chain length vs. monomer concentration (Fig. 10) were linear with both $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators. The dependence of the rate of polymerization on monomer concentration for methyl methacrylate and acrylonitrile monomers and $\text{Fe}^{3+}\text{OH}^-$ initiator, hitherto not reported, has also been studied and is illustrated in Fig. 11.

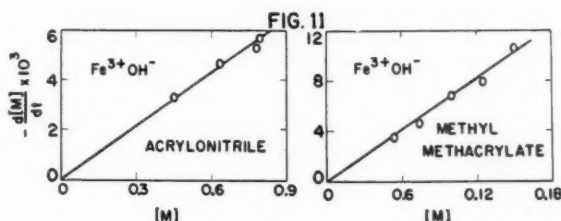
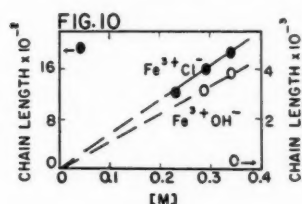


FIG. 10. Chain length of polymethyl acrylate as a function of concentration of monomer.

FIG. 11. Rates of polymerization of acrylonitrile and methyl methacrylate with $\text{Fe}^{3+}\text{OH}^-$ initiator as functions of concentration of monomer.

(d) *Quantum Yields for Production of Ferrous Ion*

The maximum quantum yields for production of ferrous ion at 30°C ., measured at monomer concentrations corresponding to their solubility in the aqueous medium, were found to depend on the initiating species and the wavelength of the radiation (Table I). With $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators the quantum yields were practically equal at 3130 and 3650 Å but dropped off steeply when the limit of the visible was reached. It is, however, of interest that γ_{max} reported (9) for $\text{Fe}^{3+}\text{OH}^-$ (0.05) and $\text{Fe}^{3+}\text{Cl}^-$ (0.13) in the presence of methyl methacrylate and acrylonitrile were not realized in the presence of methyl acrylate. The quantum yields with regard to monomer disappearance were found to depend on monomer concentration, light intensity, etc.

(e) *Effect of Initially Added Ferrous Ion and Ferrous Ion Formed During the Reaction*

The rate of increase of ferrous ion concentration was found to be considerably reduced by (i) initially added ferrous ions and (ii) ferrous ions accumulating in the course of the reaction. The reciprocal rate of formation of ferrous ion with $\text{Fe}^{3+}\text{Cl}^-$ initiator was found to vary linearly with the mean ferrous ion concentration in the system. Linear relationships were also observed in the plots of reciprocal rate of increase of ferrous ion concentration vs. mean ferrous ion concentration with the systems $\text{Fe}^{3+}\text{OH}^-$ - methyl methacrylate and $\text{Fe}^{3+}\text{Cl}^-$ - methyl acrylate (Fig. 12). The mean ferrous ion concentration was taken to be the sum of the initial ferrous ion concentration and half the increase in concentration of ferrous ions resulting from the reaction.

DISCUSSION

Application of stationary state kinetics to the reaction scheme leads to the following expression for the rate of formation of ferrous ion:

$$\frac{d[\text{Fe}^{2+}]}{dt} = \frac{k_4 I}{k_d + k_s + k_i'[\text{M}]} \left(\frac{k_s k_i [\text{M}]}{k_0 [\text{Fe}^{2+}] + k_i [\text{M}]} + k_i' [\text{M}] \right).$$

The fact that the quantum yield for ferrous ion production reached a constant value below unity at the highest monomer concentration provides evidence that the undissociated complex, Fe^{2+}X , does not initiate polymerization directly, or, more accurately,

that $k_i'[M] \ll k_s$. The above equation can therefore be simplified to:

$$[1] \quad \frac{d[Fe^{2+}]}{dt} = \frac{k_s k_e I}{k_d + k_s} \left(\frac{k_i [M]}{k_i [M] + k_0 [Fe^{2+}]} \right)$$

Thus when OH or Cl free radicals initiate polymerization the quantum yield, defined by $(d[Fe^{2+}]/dt)/k_e I$, has, according to equation [1], the maximum value $k_s/(k_d + k_s)$.

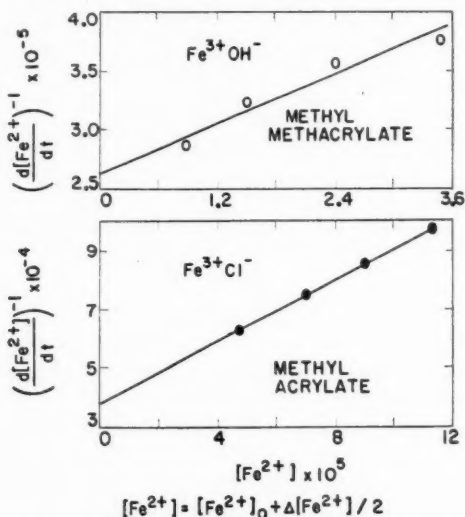


FIG. 12. Rate of accumulation of ferrous ion as a function of mean concentration of ferrous ion.

Equation [1] was applied to the experimental results in the following ways:

(i) The variation of $d[Fe^{2+}]/dt$ with k_e for both the complexes was found to be linear (Fig. 1).

(ii) The influence of ferrous ion produced during the course of the reaction or of ferrous ion initially added has been tested by plotting $(d[Fe^{2+}]/dt)^{-1}$ against $[M]^{-1}$ and against $[Fe^{2+}]$ (Figs. 12 and 8). From the slopes of these plots the ratio k_0/k_i was evaluated. The value of the ratio for the system methyl acrylate - $Fe^{3+}OH^-$ is 1.26×10^4 while for methyl acrylate - $Fe^{3+}Cl^-$ it is 3.8×10^3 . The intercepts of these graphs give the values of $k_s/(k_d + k_s)$ as 0.024 for $Fe^{3+}OH^-$ and 0.14 for $Fe^{3+}Cl^-$. These values are of the expected orders of magnitude, though it may be noted that $\gamma = k_s/(k_d + k_s) = 0.14$ for $Fe^{3+}Cl^-$ is not in accord with the value 0.078 determined by direct measurement of $d[Fe^{2+}]/dt$ at maximum concentration of monomer (Table I). In view of the fact that small experi-

TABLE I
QUANTUM YIELDS FOR FERROUS ION PRODUCTION WITH
 $Fe^{3+}OH^-$ AND $Fe^{3+}Cl^-$ INITIATORS

Wave length, angstroms	Quantum yield	
	$Fe^{3+}OH^-$	$Fe^{3+}Cl^-$
3130	0.033	0.078
3650	0.022	0.075
4050	0.015	0.044
4360	0.017	0.047

mental errors in the determination of mean ferrous ion concentration introduce large errors in the graphical evaluations of k_0/k_t and $k_s/(k_d+k_s)$ the estimation of these quantities must be regarded as only approximately correct. The value of $k_s/(k_d+k_s)$ for $\text{Fe}^{3+}\text{Cl}^-$ may be considered higher than the correct value by a factor of 2.

It may be stated here that the quantum yields for ferrous ion production higher than our values have been reported by Baxendale and Magee (14) and by Dainton (15) in their works on the reactions of organic free radicals with species involving ferrous and ferric ions. Baxendale's values (14) for quantum yields for ferrous ion production in the oxidation of benzene with $\text{Fe}^{3+}\text{OH}^-$ as the active species are higher than ours by a factor of six. On the other hand the quantum yields reported by Baxendale are higher than ours only by a factor of two when we consider our quantum yields with $\text{Fe}^{3+}\text{Cl}^-$ as the active species. Baxendale's work (14) is connected with the oxidation of benzene by OH radicals from $\text{Fe}^{3+}\text{OH}^-$ in homogeneous medium whilst our work is connected with the reaction of OH radicals with vinyl monomer in a medium where the polymer continuously precipitates. We venture to suggest that the decrease in the quantum yields for ferrous ion production in our system may be due to the following reasons. Firstly we have not considered the reaction step,



suggested by Baxendale because such a step with reference to our reaction system would mean that the rate of polymerization would be proportional to the first power of light intensity. On the other hand we have observed in our polymer reactions that the rate of polymerization is always proportional to the light intensity raised to the power half which means that the termination involves two chain radicals but never a chain radical and an ion like Fe^{3+} or an ion pair like Fe^{3+}X^- ($\text{X} = \text{Cl}$ or OH), as suggested by Baxendale (14), or FeCl_3 molecule and a chain radical as suggested by Bamford (16).

Secondly Baxendale has produced evidence that the secondary back reaction $\text{Fe}^{2+} + \text{OH}^- \longrightarrow \text{Fe}^{3+} + \text{OH}^-$ is negligible in his reaction system. On the other hand the existence of this back reaction in photochemical polymerization in aqueous medium using ion pairs as photosensitizers is well established in our system and others already reported (6, 7, 8, 9). The fall in $d\text{Fe}^{2+}/dt$ with time as well as the influence of initially added Fe^{2+} on $d\text{Fe}^{2+}/dt$ have provided strong evidence in favor of such a reaction. Baxendale and Magee (14) are unable to account for the imbalance between ferrous ion produced and the oxidation products of benzene but they are of the opinion that the consumption of free radicals by impurities in the system is of no importance; however, we have strong evidence in favor of the consumption of radicals by impurities in our system involving polymer formation (17).

(iii) The influence of light intensity was assessed by plotting $(d\text{Fe}^{2+}/dt)(1+(k_0[\text{Fe}^{2+}])/k_t[\text{M}])$ against the light intensity (Fig. 5), with k_0/k_t values obtained by the procedure described above.

In accordance with the reaction scheme the rate of disappearance of monomer when $k_t[\text{M}] \gg k_0[\text{Fe}^{2+}]$ is:

$$[2] \quad \frac{-d\text{M}}{dt} = \frac{k_p}{k_t^{1/2}} \left(\frac{k_s k_t I}{k_d + k_s} \right)^{1/2} [\text{M}].$$

Figs. 2, 6, and 9 confirm the linear relationship between $-d\text{M}/dt$ and (a) $k_t^{1/2}$, (b) $I^{1/2}$, and (c) $[\text{M}]$. Termination of active polymer by OH or Cl free radicals would lead to $-d\text{M}/dt$ dependent on $[\text{M}]^2$ and independent of I . Experimental results thus appear to support the mechanism of termination by interaction of active polymer ends.

If termination of polymer by recombination is assumed the chain length, n , is given by:

$$[3a] \quad n = \frac{2k_p}{k_t} \left(\frac{k_d + k_s}{k_s k_t I} \right)^{1/2} [M]$$

or by

$$[3b] \quad n = -(2dM/dt) \div (dFe^{2+}/dt).$$

Values of n found by viscosity measurements are compared with those calculated from equation [3b] in Table II. The satisfactory agreement between the observed and

TABLE II
CHAIN LENGTH OF POLYMETHYL ACRYLATE INITIATED
BY $Fe^{3+}OH^-$ AND $Fe^{3+}Cl^-$

Initiator	Chain length $\times 10^{-3}$	
	Calculated (Equation 3b)	Observed (viscometry)
$Fe^{3+}Cl^-$	0.69	0.94
	0.93	1.24
	3.30	3.93
$Fe^{3+}OH^-$	1.60	1.62
	1.91	2.36
	3.17	3.46

calculated chain lengths is strong evidence in support of the recombination mechanism for termination of polymer. The applicability of equation [3a] to the experimental results has been tested by plotting (a) n vs. $[M]$ (Fig. 10), (b) n vs. $k_t^{-1/2}$ (Fig. 3), and (c) n vs. $I^{-1/2}$ (Fig. 7), all of which gave linear relationships.

Finally, from the previous estimates of $k_s/(k_d + k_s)$, values of $k_p/k_t^{1/2}$ were calculated by various methods. The results are recorded in Table III. These values of $k_p/k_t^{1/2}$

TABLE III
 $k_p/k_t^{1/2}$ VALUES (LITER/MOLE) $^{-1/2}$ SEC. $^{-1/2}$ FOR METHYL ACRYLATE POLYMERIZATION

Initiator	Method						Mean
	$-dM/dt$ vs. $[M]$	$-dM/dt$ vs. $k_t^{1/2}$	$-dM/dt$ vs. $I^{1/2}$	n vs. $k_t^{-1/2}$	n vs. $I^{-1/2}$	n vs. $[M]$	
$Fe^{3+}OH^-$	0.432	0.402	0.392	0.77*	0.757*	0.453	0.42
$Fe^{3+}Cl^-$	0.272	0.276	0.145	0.123	0.6*	0.782*	0.20

*Not used in calculating mean.

relate to aqueous solution and it does not appear profitable to make comparisons with values reported for bulk or solution polymerization because of various factors, as yet unknown, operating in aqueous medium.

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DETERMINATION OF LEAD BY DITHIZONE IN A SINGLE PHASE WATER-ACETONE SYSTEM¹

D. G. M. DIAPER AND A. KUKSIS²

ABSTRACT

A modification of the dithizone colorimetric procedure for determination of lead has been developed. By working in an aqueous acetone system (70% acetone by volume) the usual extraction step is avoided. Aqueous ethanol or methanol may also be employed or, under suitable circumstances, water may be omitted from the solvent system. The 70% acetone system proposed is tolerant of cyanide, added to convert interfering ions into non-interfering complex ions, and the interference of copper under the conditions adopted was determined. This system was also found compatible with hydroxylamine, used as stabilizer, and with the barbitol buffer. A reproducibility of about 2% was obtained when working with standards in the range from 0 to 10 $\mu\text{g.}$ of lead and the technique was found to be sensitive to 0.1 p.p.m.

INTRODUCTION

Microchemical determination of lead by dithizone is a standard colorimetric procedure. It is based upon formation of the lead dithizonate complex, which is red, and extraction of this red color by an inert solvent, immiscible with water, such as carbon tetrachloride or chloroform (4).

In the course of some studies of solubilities of organic lead salts in organic solvents, it became obvious that this determination could be greatly simplified by colorimetric measurement of a one-phase system, thus eliminating the extraction step. Such a mono-phase water-cellosolve system for determination of zinc has been proposed by Vallee (6), who suggests that other solvents and other ions may be so treated. We have found that the solvent system consisting of 70% of acetone and 30% of water by volume (70% acetone) is suitable for many routine purposes, as it dissolves reasonable concentrations of complexing salts and buffer, but where such additives are unnecessary, the pure organic solvent may be used and reliable results obtained.

Acetone is readily available in high purity and dissolves large quantities of dithizone rapidly, giving solutions which may be stored for several days, without extraordinary precautions, with little loss in optical density (8). The lead dithizonate is formed immediately in pure or aqueous acetone. Pure or aqueous ethanol or methanol was also suitable.

EXPERIMENTAL AND RESULTS

Clean glassware and distilled water were used. No particular precautions were taken to ensure absolute absence of traces of metals in either the distilled water or the glassware. Small quantities of metals possibly present were to be compensated for in the optical density measurements by using an appropriate blank (3).

Color Reagent

A 0.01% solution of dithizone (British Drug Houses Laboratory Chemical) was prepared in ordinary reagent grade acetone (Merck and Co.). Before use this solution was diluted with distilled water to a final acetone concentration of 70% by volume.

Buffer and Complexing Solution

Three grams of reagent grade potassium cyanide (Fisher Reagent), 3 g. of reagent

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grade hydroxylamine hydrochloride (Baker's Analyzed), and 3 g. of barbitol sodium (Merck and Co.) were dissolved in 300 ml. of distilled water and diluted to 1 liter with acetone. Hydrochloric acid, 3 *N*, was added to bring the apparent pH of this acetone solution to 5.5.

If necessary, lead and other heavy metals may be removed by extracting the neutral aqueous salt solution with dithizone dissolved in carbon tetrachloride.

Lead Standards

Reagent grade lead nitrate or lead acetate (Fisher Certified Reagent) was dried to constant weight and assayed by the lead molybdate method (7). They were found to be respectively 99.3 and 99.6% pure. Each was dissolved in distilled water at room temperature and diluted with acetone to a final lead concentration of 5 μ g. per ml. in 70% acetone.

Preparation of Samples for Analysis

The following method is a modification of that of Cook (2) and was used for the determination of lead in organic polymer samples containing minute amounts of lead stearates.

To 250–500 mg. of the sample in a 250-ml. Kjeldahl flask, 25–50 ml. of distilled nitric acid was added and the suspension gently boiled so as to evaporate the solution to near dryness within 30 to 45 minutes. Then the flask was cooled and 5 ml. of 1:1 nitric acid together with 1–2 ml. of lead-free 70% perchloric acid added and the solution boiled gently till white fumes appeared. The heat was reduced and the digestion continued barely at the boiling point till the solution turned completely colorless. After cooling, the contents of the flask was diluted with distilled water, neutralized with dilute ammonium hydroxide, and made up to volume, usually 1 liter. Portions of this solution were diluted to 70% acetone, and suitable aliquots of this aqueous acetone solution taken for the colorimetric analysis.

When lead acetate standards were treated in a similar manner quantitative recoveries were obtained.

Apparatus

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer, with 1.000 cm. matched silica cells. A constant sensitivity was maintained by use of variable slit widths. The absorption curves for the dithizone and the lead dithizonate solutions were obtained with a Beckman Model DK 2 recording spectrophotometer, using the same cells.

The pH measurements were made with a Beckman Model N glass electrode pH meter. The meter was frequently standardized against a Beckman buffer, pH 7.00. The electrodes were exposed to the acetonic solution only for short periods of time and thoroughly washed and soaked in water after each exposure.

Procedure

Into a 25-ml. volumetric flask were placed from a 50-ml. burette 10 ml. of the buffer and complexing solution, 10 ml. of the color reagent, and from a 10-ml. burette the neutral unknown or standard in 70% acetone solution, and the volume made up to 25 ml. with 70% acetone. For this particular amount of dithizone used, the sample should not contain more than 10 μ g. of lead. The contents of the flasks were mixed by inversion. The lead dithizonate was formed immediately and the optical density could be measured. The readings should be completed within some 15 minutes, as the color on standing slowly fades.

In order to select the wave length at which maximum sensitivity would be obtained, absorption curves for dithizone and the lead dithizonate separately were recorded.* The curves obtained, together with the experimental details, are shown in Figs. 1-4. The shifts in the wave lengths of maximum and minimum absorption, as well as changes in extinction under a variety of experimental conditions, are listed in Table I.

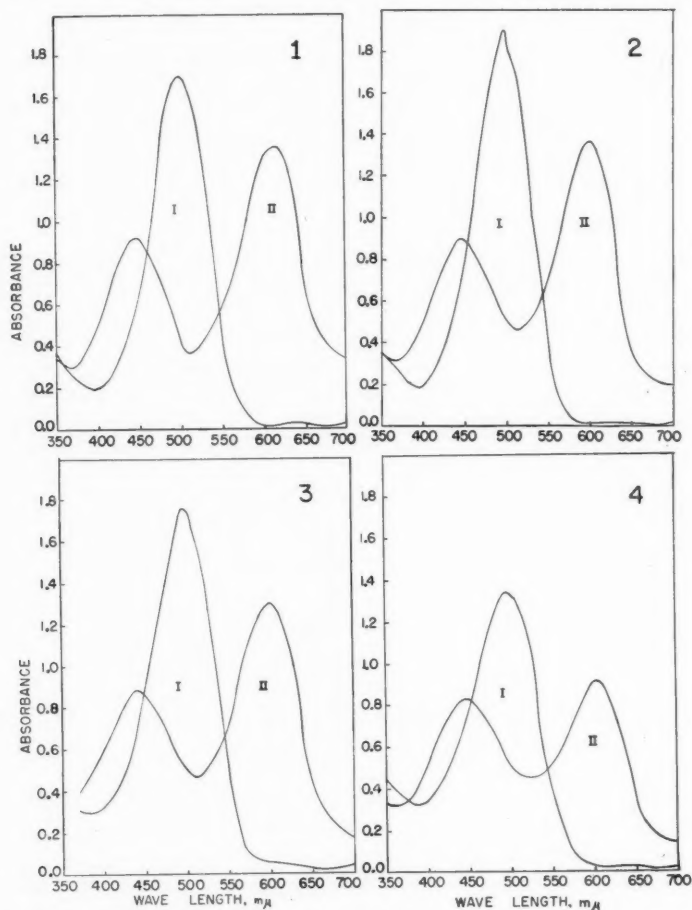


FIG. 1. Spectrophotometric absorption curves in pure acetone. I—Lead dithizonate. II—Dithizone.

FIG. 2. Spectrophotometric absorption curves in 70% acetone. I—Lead dithizonate. II—Dithizone.

FIG. 3. Spectrophotometric absorption curves in 70% acetone in the presence of buffer and complexing salts. (See Table I.) I—Lead dithizonate. II—Dithizone.

FIG. 4. Spectrophotometric absorption curves in 70% acetone in the presence of buffer and complexing salts. (See Table I.) I—Lead dithizonate. II—Dithizone.

Two wave lengths, 500 $m\mu$ (at which the minimum for dithizone and the maximum for the dithizonate are approximately located) and 600 $m\mu$ (at which dithizone has its second maximum and the dithizonate a very low absorption), were chosen. When

*The authors thank Dr. J. D. Jones, Department of Biology, Queen's University, Kingston, Ontario, for making the spectrophotometric recordings.

TABLE I
SPECTROPHOTOMETRIC BEHAVIOR OF DITHIZONE AND LEAD DITHIZONATE IN ACETONE,
AND ACETONE AQUEOUS MIXTURES^a

Solvent	Apparent pH of system	Dithizone (m μ)					Dithizonate (m μ)			
		Max. I	Max. II	Min.	Max. II ^d		Max. I	Max.	Min.	Max. ^d
					Min.	Max. II ^d				
Acetone	—	447	615	513	3.6	1.5	499	393		8.5
70% Acetone	—	445	599	513	3.0	1.5	495	391		10.0
70% Acetone, buffer, salts ^b	5.5	444	600	516	2.8	1.5	495	388		5.8
70% Acetone, buffer, salts ^c	5.5	443	600	523	2.0	1.1	495	383		4.2

^a Approximately 0.63 mg. of dithizone was present per 25 ml. of solution in all of the determinations.

^b Barbital buffer, hydroxylamine hydrochloride, and cyanide in concentrations as described in the procedure.

Fig. 3.

^c Barbital buffer, hydroxylamine hydrochloride, and cyanide in concentrations three times those described in the procedure. Fig. 4.

^d Absorbance ratios.

the measurements were taken at 500 m μ , the reference solution, in order to compensate for the absorption of the dithizone, was composed of the same ingredients as the sample solution, except that the lead solution was replaced by 70% acetone. For measurements at 600 m μ , the reference solution, in order to compensate for the absorption of the lead dithizonate, was changed to contain an excess of the lead solution to convert all dithizone completely into the lead dithizonate.

Though the measurement at 600 m μ is more sensitive, owing to the greater optical density difference (see Figs. 1–4), this advantage is lost since a new standard curve has to be prepared every day, as the dye solution slowly fades on standing overnight. The standard curve obtained from measurements of the dithizonate absorption at 500 m μ , on the other hand, serves from day to day until the buffer supply is exhausted, when a new curve for the new buffer should be prepared.

At both wave lengths straight line relationships between the lead concentration and the optical density were obtained, indicating that the Beer-Lambert law was obeyed; hence the lead concentration in the sample could be read directly off the graph. The calibration curves obtained are illustrated in Fig. 5.

Estimation of Reliability

The results of analyses of eight consecutive series of lead standards are shown in

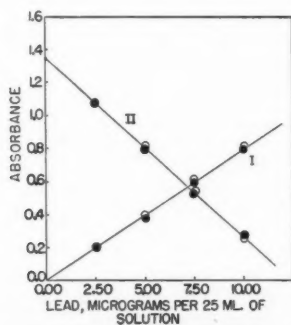


FIG. 5. Calibration curves for lead in 70% acetone solution containing buffer and complexing salts. I—Determinations performed at 500 m μ . II—Determinations performed at 600 m μ .

Table II. For the analysis of variance (9) each figure of this table was proportionally reduced to the 5 $\mu\text{g.}$ level and, after observing that the standard deviations for the data obtained with the two methods of measurement were equal, the figures were combined. The 32 observations were arranged in four sets according to the original lead concentration levels. It was found that the average difference between duplicates was 0.11% and the coefficient of variation 1.93%.

TABLE II
CONSECUTIVE ANALYSES OF SERIES OF LEAD STANDARDS

Series ^a	Lead standards, $\mu\text{g.}$			
	2.50	5.00	7.50	10.00
I	2.55	5.10	7.59	10.06
II	2.50	5.13	7.56	10.10
III	2.45	5.00	7.41	9.80
IV	2.44	4.90	7.35	9.98
V	2.46	4.95	7.68	10.28
VI	2.45	4.90	7.36	9.80
VII	2.55	4.91	7.71	9.90
VIII	2.58	5.05	7.38	9.82

^aSeries I, II, III, and IV were obtained by measuring the absorption at 500 $m\mu$, while series V, VI, VII, and VIII were obtained by measuring the absorbance at 600 $m\mu$.

Interferences

Only copper(II) was tested for its interference with the lead determination. It was found that using the cyanide concentration specified in the procedure 12.5 $\mu\text{g.}$ of copper produced an effect similar to that for 1 $\mu\text{g.}$ of lead. This interference could be further decreased by addition of more cyanide. Increasing the cyanide concentration four times permitted the addition of about 25 $\mu\text{g.}$ of copper before an effect similar to that for 1 $\mu\text{g.}$ of lead could be observed.

Sn(II), Tl(I), Bi, Hg, and Ag were also thought to interfere (4), though the actual extent of interference was not quantitatively determined, because this interference was shown to vary with the amount of cyanide present. The maximum cyanide concentration that can be used is determined by other factors, notably the acetone-water ratio and the buffer concentration selected. No systematic investigation of these variables was attempted.

Other Procedures

The formation of lead dithizonate also took place readily in acetone alone and methyl and ethyl alcohols either in the presence of water and buffer or in the absence of either or both. The color formation was quantitative and a straight line relationship between the lead concentration and the optical density was again observed.

The spectrophotometric measurements were taken either at 500 or at 600 $m\mu$ using the appropriate reference solutions. This particular method was found to be useful for the determination of the solubility of lead salts of certain fatty acids in the above-mentioned organic solvents.

DISCUSSION

In preparing the buffer and complexing solution, it will be noted that adjustment of pH is performed after acetone has been added to the aqueous salt suspension. A prior

adjustment is impossible with the concentrations employed, for barbitol, though quite soluble in the final solution, is only sparingly soluble in water.

The glass electrode was used in the adjustment and the figure obtained recorded as an "apparent pH", for, although it is a meaningful practical measurement, it is not representative of the actual hydrogen ion concentration (1). For maximum sensitivity, the limits of pH permissible in this determination are narrow. On the alkaline side of the apparent pH of 5.5 the dithizone exists predominantly as the enol form. This monovalent dithizonate ion exhibits an orange-yellow color, undesirable in the determination of lead. On the acid side, in the presence of buffer and complexing salts, it was found that the sensitivity of the color change was diminished; that is, similar quantities of lead produced significantly greater color changes at an apparent pH of 5.5 than at lower values. This may have been due to the influence of cyanide upon the dithizone-lead dithizonate equilibrium, or because of some acid-promoted decomposition of lead dithizonate. For optimum reproducibility a critical adjustment of the apparent pH of the system to 5.5 was deemed necessary. (The apparent pH of 5.5 was thought to correspond approximately to the buffering range of the barbitol, since dilute aqueous barbitol solutions, originally at pH 7.0, displayed this apparent pH when brought to 70% acetone concentration.)

The formation of the lead dithizonate is sensitive to and readily affected by the concentration of the lead ion and dithizone, pH, the character and concentration of the buffer as well as the character and concentration of the complex formers (6). Interferences may be controlled by keeping in mind the chemical nature of the ions and their concentrations likely to be encountered in the working medium.

The changes in the absorption characteristics of dithizone and lead dithizonate in aqueous organic solvents from those in the corresponding pure organic solvents and those in carbon tetrachloride (4) are significant and should be determined specially for the chosen solvent system. Though the shifts in the wave lengths of maximum and minimum absorption and the changes in the extinction at times are considerable, the general shape of the characteristic curves is always preserved. Such observations have been described before and they are in line with the findings on other dyes (5, 6).

Arbitrary selection of the 70% aqueous acetone medium was made for convenience and uniformity and it does not follow that this medium is universally applicable or even the best for the present analyses. It does, however, serve as an example of a single phase aqueous organic solvent system in which dithizone and its lead derivative, buffer, and complexing salts can all be held in solution. Other acetone and water, or acetone-alcohol-water proportions have been successfully used. At high water concentrations (above 50%) the dithizone or more often the dithizonate precipitates out.

There was little change in temperature observed when the different solutions were mixed and no precautions similar to those taken by Vallee (6) in the case of methyl cellosolve were necessary.

The buffer containing potassium cyanide was added to complex Pd, Hg, Ag, and Cu potentially present in the unknown. As was already mentioned, the extent to which this interference could be controlled depended upon the cyanide concentration used, the permissible concentration of the latter varying with the experimental system chosen. The hydroxylamine hydrochloride was added to stabilize the dithizone and the lead dithizonate, the amount added depending upon the quantity of the oxidizing agents potentially present in the working medium. The barbitol buffer was chosen because of its marked solubility in organic solvent systems. The more popular phosphate buffer for the pH range in question could not be used because of the low solubility of lead phosphate.

For optimum reproducibility, samples may be read right after mixing or up to 30 minutes later, as the color fades only slowly and the Beer-Lambert relationship is maintained. The readings should, however, be completed within some 15 minutes, as measurements taken over a period of time may differ significantly.

Though this method may have a somewhat more limited application than the conventional extraction procedures, because of its inability to perform satisfactorily under alkaline conditions and in the presence of large quantities of complexing salts, which would not dissolve in the organic solvent system, it should be definitely advantageous where applicable.

ACKNOWLEDGMENT

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THE REACTION OF ACETIC AND TRIFLUOROACETIC ANHYDRIDES WITH SOME SUBSTITUTED GUANIDINE HYDROCHLORIDES¹

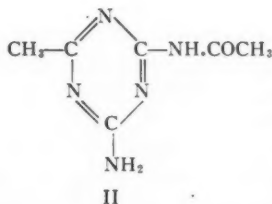
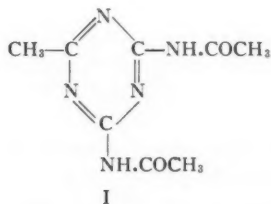
W. F. COCKBURN AND R. A. B. BANNARD

ABSTRACT

Acetylation of the hydrochlorides of guanidine, cyclohexylguanidine, and 1-guanylpiperidine has been found to yield substituted triazines. Trifluoroacetylation of 1-guanylpiperidine hydrochloride also gives a triazine, whereas guanidine hydrochloride and cyclohexylguanidine hydrochloride are converted to *bis*trifluoroacetyl derivatives. The same triazines can also be obtained by acylation of the appropriate biguanide.

During the course of a recent investigation, it became necessary to form derivatives of certain guanidine salts. To this end, a brief examination was made of the products obtained by subjecting various guanidine hydrochlorides to the action of acetic anhydride and trifluoroacetic anhydride. The results obtained form the subject of this paper.²

The acetylation of guanidine acetate with acetic anhydride was studied by Ryabinin (4), who found that the product obtained depended on the reaction conditions used and the method of working up. Relatively mild conditions (heating at 100°) yielded diacetylguanidine, while treatment with excess acetic anhydride at reflux temperatures gave 2,4-diacetamido-6-methyl-1,3,5-triazine (I). The latter was readily hydrolyzed by recrystallization from water to 2-acetamido-4-amino-6-methyl-1,3,5-triazine (II) which could be reacylated to I. Repeated recrystallization of diacetylguanidine from 95% ethanol gave acetylguanidine acetate, which yielded I on treatment with boiling acetic anhydride.



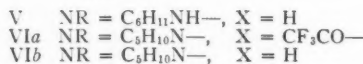
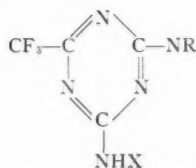
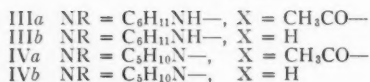
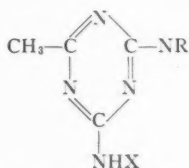
The compounds used in the present investigation were the hydrochlorides of guanidine, cyclohexylguanidine, and 1-guanylpiperidine. The dried, powdered salts were stirred under reflux with a moderate excess of anhydride for several hours, the reaction mixture concentrated by vacuum evaporation, and the products purified by crystallization and sublimation. In two cases only, namely the reaction between trifluoroacetic anhydride and the hydrochlorides of guanidine and cyclohexylguanidine, were simple diacetylguanidines obtained. The other reactions all yielded substituted triazines of the type described by Ryabinin (4). Thus, acetylation of guanidine hydrochloride, cyclohexylguanidine hydrochloride, and 1-guanylpiperidine hydrochloride gave 2,4-diacetamido-6-methyl-1,3,5-triazine (I), 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa), and 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa) respectively, while trifluoro-

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²It should be noted that, in some cases, no attempt was made to establish maximum yields.

acetylation of 1-guanylpiperidine hydrochloride gave 4-amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb).



On being heated with dilute aqueous methanolic alkali, the amides IIIa and IVa underwent ready hydrolysis to the corresponding amines IIIb and IVb. The latter were themselves quite stable to prolonged reflux in the same alkaline medium. The amine VIb was easily further trifluoroacetylated to VIa, which in turn could be hydrolyzed back to the amine under mild alkaline conditions. Trifluoroacetylation of V yielded an unstable product which could not be obtained sufficiently pure for characterization.

In order to confirm the triazine structure assigned to these products, they were synthesized by the method of Curd, Landquist, and Rose (2), from the appropriate biguanides, which were themselves prepared by the interaction of an amine with dicyandiamide in the presence of copper sulphate (3). Thus, acetylation of cyclohexylbiguanide and *N,N*-pentamethylenebiguanide gave IIIa and IVa respectively, while trifluoroacetylation of the same compounds yielded V and VIa. Identity with the compounds obtained by acylation of the guanidine salts was in all cases confirmed by melting point, mixed melting point, and infrared spectrum.

The fact that trifluoroacetylation of guanidine and cyclohexylguanidine hydrochlorides yielded *bistrifluoroacetyl* compounds rather than triazines could conceivably be due to the low reflux temperature of trifluoroacetic anhydride. Indeed, it is reported that acetylguanidine undergoes self-condensation to 2,4-diamino-6-methyl-1,3,5-triazine on being heated at 190–210° for 30 minutes (5). To check this possibility, *bistrifluoroacetyl*-cyclohexylguanidine was heated in a sealed tube (to prevent sublimation) at 140° for 1 hour. A quantitative recovery of starting material was obtained. Heating at 200° for 30 minutes caused some decomposition, but 52% of the starting material was recovered, and no evidence of triazine formation noted. Finally, cyclohexylguanidine hydrochloride was heated in a sealed tube at 140° for 2 hours, with trifluoroacetic anhydride. *Bistrifluoroacetyl*-cyclohexylguanidine was obtained in 86% yield, and again no triazine could be detected.

The ultraviolet spectra of all products, in the range 200–400 mμ, were measured, as an approximately 0.002% solution in cyclohexane or ethanol, using a 0.5 cm. quartz cell (see Table I).

For purposes of comparison, the trifluoroacetyl derivatives of *n*-butylamine, 3-diethylaminopropylamine, ethylenediamine, and piperidine were prepared, but found to give only end absorption.

EXPERIMENTAL

All melting points are corrected unless otherwise stated. Microanalyses are by Microtech Laboratories, Skokie, Ill., and by C. E. Reynolds of these laboratories. Infrared

TABLE I
 ULTRAVIOLET ABSORPTION MAXIMA OF ACETYLATION AND TRIFLUOROACETYLATION PRODUCTS

Compound	λ_{\max}	ϵ_{\max}
4-Amino-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIb)	207	27,400
	257	3,900
4-Acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa)	221	32,200
	266	2,020
4-Amino-6-methyl-2-piperidino-1,3,5-triazine (IVb)*	213	21,300
	225	18,200
	263	4,160
4-Acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa)	228	32,300
	273	2,870
4-Amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V)	207.5	24,500
	271	3,290
4-Amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb)	206.5	18,800
	227	22,600
	277	3,310
4-Acetamido-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIa)	232	18,800
	246	18,500
	290	1,650
	214	4,830
Bistrifluoroacetylguanidine	258	11,500
	229	8,540
	236	8,090
	267	11,900

*In ethanol. All others in cyclohexane.

spectra were measured on a Baird Double Beam Recording Spectrophotometer, while the ultraviolet spectra were taken on a Cary Model 14 P.M. Recording Spectrophotometer.

1-Guanylpiperidine (Ref. 1)

An aqueous suspension of methylisothiurea sulphate was treated with two molecular equivalents of piperidine, and the mixture heated on the steam bath until evolution of mercaptan had ceased. 1-Guanylpiperidine sulphate commenced to crystallize out before the end of the reaction, and was purified by recrystallization from water. It was obtained in colorless prisms, m.p. 294.5° (uncorr.) with decomp., when the sample was inserted into the melting point apparatus at 285°. Yield, 43%. Found: C, 40.80, 40.91; H, 7.98, 8.17; N, 24.15, 24.15%. Calc. for $C_{12}H_{28}N_6O_4S$: C, 40.90; H, 8.01; N, 23.85%.

The sulphate was converted to the hydrochloride by passing an aqueous solution through a column of IRA-400 (Cl^-), and the product purified by recrystallization from a mixture of ethanol and acetone, being obtained as prismatic needles, m.p. 184–186°. Found: C, 44.52; H, 8.74; N, 25.18; Cl, 21.69%. Calc. for $C_6H_{14}N_3Cl$: C, 44.03; H, 8.62; N, 25.68; Cl, 21.67%.

A portion of the hydrochloride was converted to the free base by passage in ethanolic solution through a column of IRA-400 (OH^-) resin. The base, obtained by evaporation of the eluate to dryness *in vacuo*, was purified by sublimation at 80° and 0.001 mm. The sublimate consisted of colorless crystals, m.p. 145.5–147°, which dissolved in water to give a strongly alkaline solution. Found: C, 57.00, 57.03; H, 9.88, 10.08; N, 32.93, 33.12%. Calc. for $C_6H_{13}N_3$: C, 56.66; H, 10.30; N, 33.05%.

Cyclohexylguanidine

Cyclohexylguanidine sulphate was prepared from cyclohexylamine in a similar manner

as the above. Owing to its high solubility in water and ethanol, the sulphate could not be separated from the sparingly soluble cyclohexylamine sulphate. It was therefore passed in aqueous solution through a column of IRA-400 (OH^-) to convert it to the free base, and adsorbed on a column of IRC-50 (H^+). Elution with hydrochloric acid followed by evaporation of the acid solution *in vacuo* yielded the hydrochloride. The latter was purified by recrystallization from ethanol and yielded stubby needles, m.p. 224–226°. Found: C, 47.56; H, 8.85; N, 23.40; Cl, 19.80%. Calc. for $\text{C}_7\text{H}_{16}\text{N}_3\text{Cl}$: C, 47.32; H, 9.08; N, 23.65; Cl, 19.96%. The over-all yield was not accurately determined, but was approximately 20%, mainly because of losses on crystallization.

A portion of the hydrochloride was reconverted to the sulphate by passage in solution down a column of IRA-400 (SO_4^{2-}), and the product purified by recrystallization from ethanol. The m.p. was 273° (uncorr.) with decomp. Found: C, 44.48, 44.39; H, 8.86, 8.57; N, 21.64, 21.83; S, 8.58, 8.56%. Calc. for $\text{C}_{14}\text{H}_{32}\text{N}_6\text{O}_4\text{S}$: C, 44.19; H, 8.48; N, 22.09; S, 8.43%.

N,N-Pentamethylenebiguanide

The general method of Curd and Rose (3) was followed, namely, the interaction of piperidine and dicyandiamide in the presence of copper sulphate. The product was obtained in 26% yield as the dihydrochloride, m.p. 213–217° with decomp. Found: C, 34.94, 34.84; H, 7.05, 7.17; N, 29.46, 29.18; Cl, 28.87, 28.90%. Calc. for $\text{C}_7\text{H}_{17}\text{N}_5\text{Cl}_2$: C, 34.72; H, 7.08; N, 28.93; Cl, 29.28%.

The free base was gummy and unsuitable for analysis.

Cyclohexylbiguanide

A similar reaction with cyclohexylamine yielded cyclohexylbiguanide dihydrochloride, m.p. 225° with decomp. Found: C, 37.45; H, 7.57; N, 27.63; Cl, 27.05%. Calc. for $\text{C}_8\text{H}_{19}\text{N}_5\text{Cl}_2$: C, 37.52; H, 7.47; N, 27.34; Cl, 27.68%. The dihydrochloride was converted to the free base by treatment in ethanolic solution with a twofold excess of silver oxide, removal of the silver salts by filtration, and evaporation of the filtrate to dryness. The base was a crystalline solid, m.p. 196–205° with decomp. Found: C, 43.87; H, 8.26; N, 31.78%. Calc. for $\text{C}_8\text{H}_{21}\text{N}_5\text{O}_2$: C, 43.81; H, 9.65; N, 31.94%. These figures indicate that the base was obtained as a dihydrate.

Trifluoroacetyl Derivatives of Amines

The amines were treated with trifluoroacetic anhydride in ether. Water was added to the reaction mixture, and the product solvent-extracted and distilled in the case of the liquid amides, or filtered off and recrystallized from aqueous ethanol in the case of the solid amide.

1-Trifluoroacetylaminobutane.—This colorless, mobile oil with an ester-like odor was purified by distillation in a Späth bulb at 9 mm. pressure, and an air-bath temperature of 100°, n_D^{25} 1.3803. Found: C, 43.23; H, 6.11; N, 8.37%. Calc. for $\text{C}_6\text{H}_{10}\text{NF}_3\text{O}$: C, 42.60; H, 5.96; N, 8.28%.

N-Trifluoroacetyl-N',N'-diethyl-1,3-diaminopropane.—Colorless oil with an amine-like odor, distilled in a Späth bulb at 7 mm. pressure and an air-bath temperature of 130°, n_D^{25} 1.4183. Found: C, 47.67; H, 7.36; N, 12.70%. Calc. for $\text{C}_9\text{H}_{17}\text{N}_2\text{F}_3\text{O}$: C, 47.77; H, 7.57; N, 12.39%.

N,N'-Bistrifluoroacetyl-1,2-diaminoethane.—This amide was obtained as a white, non-wettable, crystalline solid, m.p. 200–201°. Found: C, 28.83; H, 2.41; N, 10.92%. Calc. for $\text{C}_6\text{H}_6\text{N}_2\text{F}_6\text{O}_2$: C, 28.59; H, 2.40; N, 11.11%.

Trifluoroacetyl piperidine.—Colorless oil with a penetrating odor of peppermint, b.p. 77° at 15 mm. pressure, n_D^{25} 1.4148. Found: C, 46.52, 46.42; H, 5.68, 5.80; N, 7.87, 7.82%. Calc. for $C_7H_{10}NF_3O$: C, 46.41; H, 5.56; N, 7.73%.

Reactions with Acetic Anhydride

Guanidine Hydrochloride

Guanidine hydrochloride (6.0 g.) and acetic anhydride (100 ml.) were heated under reflux with stirring for 2 hours. The undissolved guanidine hydrochloride (2.65 g.) was filtered off, and the red filtrate concentrated to 50 ml. On cooling to 15°, the solution deposited yellowish crystals, which were filtered off, washed with ether, and dried for several days *in vacuo* over potassium hydroxide. Weight, 2.07 g. Concentration of the mother liquor yielded a further 0.62 g. Both materials gave a negative test for chloride ion. They were combined and recrystallized from ethyl acetate, yielding 1.47 g. (40%) of colorless crystals, m.p. 209–213.5°. Rapid heating from 200° gave a melting point of 214–216° C. (uncorr.) with decomp. The m.p. of 2,4-diacetamido-6-methyl-1,3,5-triazine (I) is reported to be 217.5° (1). Found: C, 45.68, 45.71; H, 5.28, 5.24; N, 33.06, 32.93%. Calc. for $C_8H_{11}N_5O_2$: C, 45.94; H, 5.30; N, 33.48%.

Cyclohexylguanidine Hydrochloride

The guanidine salt (311 mg.) was refluxed with acetic anhydride (15 ml.) with stirring for 10 hours. The excess anhydride was distilled off under vacuum, and the brown residue recrystallized from acetone, using decolorizing charcoal. Yield of 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa), 64 mg. (35%), m.p. 188–189°. Found: C, 57.74; H, 7.69; N, 28.11%. Calc. for $C_{12}H_{19}N_5O$: C, 57.81; H, 7.68; N, 28.09%.

This amide (90 mg.) was dissolved in 4 ml. of hot methanol, 0.5 ml. of 2.5 *N* sodium hydroxide solution was added, and the solution refluxed for 1 hour. The hot solution was filtered from a small amount of flocculent material, and concentrated to 1 ml. *in vacuo*. A crystalline solid suddenly precipitated, and was filtered off and washed with water. Yield of IIIb, 75 mg., m.p. 185–186°. A strong depression in melting point was obtained on admixture with the starting material. Found: C, 57.85; H, 8.26; N, 33.78%. Calc. for $C_{10}H_{17}N_5$: C, 57.94; H, 8.27; N, 33.79%.

1-Guanylpiperidine Hydrochloride

This reaction was similar to the previous one. The product was purified by recrystallization from acetone–petroleum ether, followed by sublimation at 110° and 0.02 mm. pressure, and was obtained as colorless crystals, m.p. 145–147°. Yield of 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa), 20%. Found: C, 56.68, 56.54; H, 7.12, 7.31; N, 30.10, 29.86%. Calc. for $C_{11}H_{17}N_5O$: C, 56.15; H, 7.28; N, 29.77%.

Cyclohexylbiguanide

Cyclohexylbiguanide dihydrate was refluxed in acetic anhydride for 2½ hours, and the reaction solution diluted with twice its own volume of water. The product was filtered off and recrystallized from acetone. Yield of 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa) 27%, m.p. 189–190.5°. A mixture with the product, m.p. 188–189°, of the acetylation of cyclohexylguanidine hydrochloride melted at 189–190°. Identity was confirmed by a comparison of the infrared spectra.

N,N-Pentamethylenebiguanide

Pentamethylenebiguanide dihydrochloride (1.21 g.) was converted to the free base by shaking with 3 g. of silver oxide in 75 ml. of ethanol. The slightly gummy solid obtained by evaporation of the ethanol solution was refluxed overnight with 40 ml. of acetic

anhydride, yielding a brown solution. This was treated with decolorizing charcoal, filtered, and the filtrate evaporated to dryness *in vacuo*. The residue (1.1 g.) was recrystallized twice from acetone (10 ml., then 5 ml.) using decolorizing charcoal, to give 0.52 g. (44%) of colorless crystals of 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa), m.p. 146–146.5°. No depression in melting point was obtained on admixture with the product, m.p. 146–147°, of acetylation of 1-guanylpiperidine hydrochloride, and both compounds yielded identical infrared spectra.

This acetamidotriazine (106 mg.) was dissolved in 2 ml. of methanol containing 1 ml. of water by gentle warming. Five drops of 2.5 *N* sodium hydroxide was added and the solution boiled for 5 minutes, the methanol being allowed to distill off. The product crystallized spontaneously, and was filtered off and washed with water. Yield of IVb, 83 mg. (95%), m.p. 185–187°. Found: C, 55.99, 55.75; H, 7.65, 7.68; N, 35.76, 35.47%. Calc. for $C_9H_{15}N_5$: C, 55.93; H, 7.82; N, 36.24%.

Reactions with Trifluoroacetic Anhydride

Guanidine Hydrochloride

Guanidine hydrochloride (2 g.) was stirred under reflux with 10 ml. of trifluoroacetic anhydride for 17 hours. The resulting clear yellow solution was evaporated at 60° and 12 mm. pressure to an oil (5.1 g.). Addition of 15 ml. of anhydrous ether caused part of the oil to dissolve, leaving a crystalline residue, which was filtered off and washed with ether, yielding 1.3 g. of white crystals, m.p. 155–158°. This was proved by mixed melting point and infrared spectrum to be guanidine trifluoroacetate (36% recovered).

The filtrate was evaporated to an oil *in vacuo*, and heated in a wide tube at 70° and 0.01 mm. pressure. There was obtained a colorless oil in the cooler part of the tube and, partially mixed with it, a white crystalline solid in the lower part of the tube. The tube was inverted to allow the oil to drain off, and the crystalline sublimate gently warmed to drive off the last traces of oil. The solid weighed 1.29 g., m.p. 78–81°. This material tended to become mushy on being left in a stoppered vial overnight. Two more sublimations in a horizontal tube raised the m.p. to 82–83.5°, the material being then quite stable. Found: C, 23.72, 24.09; H, 1.37, 1.41%. Calc. for $C_6H_5N_3F_6O_2$: C, 23.92; H, 1.20%.

Pure *bistrifluoroacetylguanidine* is not hygroscopic; in fact it forms a non-wettable film on the surface of water, which nevertheless rapidly acquires an acid reaction due to hydrolysis. The yield was 40%, based on recovered material.

The colorless oil obtained from the first distillation described above was redistilled in a Späth bulb at 12 mm. pressure and an air-bath temperature of 120°. Found: C, 24.72; H, 1.34. This is close to the figures for *bistrifluoroacetylguanidine*, and the oil could conceivably be an isomeric form. However, it was not conclusively identified.

Cyclohexylguanidine Hydrochloride

The reaction mixture obtained by refluxing cyclohexylguanidine hydrochloride in excess trifluoroacetic anhydride for 27 hours was concentrated *in vacuo* to a yellow oil. This was dissolved in a few milliliters of anhydrous ether, and the solution filtered from a fine crystalline precipitate, which proved to be cyclohexylguanidine trifluoroacetate, m.p. 204–206.5° (9% recovery). The ether solution was again concentrated, leaving an oily residue, which crystallized on being left overnight, m.p. 55–59°. Sublimation at 50° and 0.02 mm. pressure gave a white crystalline solid, m.p. 61–62°. Yield of *bistrifluoroacetylcyclohexylguanidine*, 89%. Found: C, 39.71, 39.53; H, 3.85, 3.93%. Calc. for $C_{11}H_{13}N_3F_6O_2$: C, 39.65; H, 3.93%.

This compound could be readily hydrolyzed in aqueous methanolic alkali to cyclohexylguanidine trifluoroacetate. However, it was quantitatively recovered unchanged after being heated in a sealed tube at 140° for 1 hour. Heating for 30 minutes at 200° caused some decomposition to an oil, only 52% of the *bistrifluoroacetyl*cyclohexylguanidine being recovered. It is unlikely that this oil is a triazine, as the compound which might be expected as a result of cyclization, 4-amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V), is a solid, m.p. 165–168° (see below).

The reaction was also carried out by heating 0.5 g. of cyclohexylguanidine hydrochloride with 10 ml. of trifluoroacetic anhydride in a sealed tube at 140° for 2 hours. *Bistrifluoroacetyl*cyclohexylguanidine was obtained in 86% yield and, again, no evidence of triazine formation was obtained.

1-Guanylpiperidine Hydrochloride

One gram of this salt was refluxed with 15 ml. of anhydride for 18 hours, and the excess anhydride removed by distillation *in vacuo*. The oily residue was dissolved in 15 ml. anhydrous ether, and the solution filtered from a white crystalline solid, 0.27 g., m.p. 234° with decomp. This was proved by analysis, and a mixed melting point with an authentic sample, to be 1-guanylpiperidinetrifluoroacetate, yield 22%.

The ether was distilled off *in vacuo*, into a dry ice trap. The contents of the trap were combined with the trap residue obtained during the distillation of excess anhydride, described above, and the mixture fractionated by means of a small Vigreux column. The oil left after removal of the more volatile anhydride and ether was distilled at 75° and 12 mm. pressure. Weight 364 mg., n_D^{25} 1.3963. Found: C, 40.56; H, 4.49; N, 5.97%. This material had the same peppermint odor as trifluoroacetyl piperidine, and gave an infrared spectrum which was virtually identical, except for a sharp peak at 1800 cm^{-1} , which could indicate persistent contamination with trifluoroacetic anhydride. This would also account for the low analysis figures. Yield, as trifluoroacetyl piperidine, 33%.

The residue from the ether solution was crystallized from ether–petroleum ether, giving 264 mg. of colorless prisms, m.p. 160°. This material could be readily vacuum-sublimed unchanged. Found: C, 44.11; H, 4.95; N, 27.91%. Calc. for $\text{C}_9\text{H}_{12}\text{N}_6\text{F}_3$: C, 43.72; H, 4.89; N, 28.33%. This substance, 4-amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb), could be further trifluoroacetylated by refluxing with excess anhydride for 90 minutes. The crystalline residue, m.p. 94–96°, obtained by evaporation of the excess anhydride, was purified by vacuum sublimation at 80° and 0.05 mm. pressure. Yield 95%, m.p. 107.5–108.5°. Found: C, 38.70; H, 3.63; N, 20.77%. Calc. for $\text{C}_{11}\text{H}_{11}\text{N}_6\text{F}_3\text{O}$: C, 38.49; H, 3.23; N, 20.41%. This amide (VIa) was very readily hydrolyzed by cold aqueous methanolic alkali back to the aminotriazine (VIb), m.p. 160°.

The mother liquors from the crystallization of VIb were evaporated to dryness, and the residue sublimed at 120° and 0.005 mm. pressure. This yielded in the hotter part of the tube a further 148 mg. of VIb (total yield 55%) and in the cooler part 46 mg. of crystals, m.p. 90–91°. Found: C, 40.58, 40.12; H, 3.49, 3.42; N, 18.11%. No reasonable structure has been found to fit this analysis.

The same products were obtained when free guanylpiperidine base was used as starting material.

Cyclohexylbiguanide

The reaction was carried out as above. Removal of the volatile constituents *in vacuo* left an oily residue, which was distilled in a Späth bulb at 0.01 mm. and an air-bath temperature of 150°. This yielded a yellow glass, which was crystallized from ligroin

(50–60°) in chunks. Recrystallization from ether/ligroin gave colorless crystals, m.p. 165–168°. Yield, 50%. Found: C, 46.04; H, 5.44; N, 26.35%. Calc. for $C_{10}H_{14}N_6F_3$: C, 45.97; H, 5.40; N, 26.81%. The analysis figures correspond to 4-amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V). This amine, on further treatment with trifluoroacetic anhydride, yielded an oily product which could be distilled in a Späth bulb at 100° and 0.01 mm. pressure, the distillate setting to a glass. This material appeared to decompose, however, a strong smell of trifluoroacetic acid rapidly becoming evident. No method of purification was devised.

N,N-Pentamethylenebiguanide

The product of trifluoroacetylation was sublimed at 90° and 0.05 mm. pressure, giving a white crystalline solid, m.p. 105–106°. Found: C, 38.73; 38.69; H, 3.12; 3.23; N, 19.67%. Calc. for $C_{11}H_{11}N_6F_6O$: C, 38.49; H, 3.23; N, 20.41%. Hydrolysis with aqueous methanolic alkali gave a crystalline product, m.p. 159–160°. This substance was proved by mixed melting point and infrared spectrum to be identical to VIb, m.p. 160°, obtained by trifluoroacetylation of 1-guanylpiperidine hydrochloride.

ACKNOWLEDGMENTS

The infrared spectra were taken by Dr. C. E. Hubley. Thanks are also due to Mr. H. A. Barber and Mr. A. Gray for technical assistance.

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AN IONIZATION GAUGE DETECTOR FOR GAS CHROMATOGRAPHY¹

S. A. RYCE AND W. A. BRYCE

ABSTRACT

An ionization gauge has been modified to serve as a detector for gas chromatography. A small fraction of the effluent gas from the column is diverted into the gauge through an adjustable leak. The gauge is operated under conditions such that ionization of the eluted compound only occurs, and not of the helium carrier. The ion current is amplified and displayed on a pen recorder. The gauge combines very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature.

INTRODUCTION

Thermal conductivity cells with either hot wire or thermistor sensing elements are used extensively as detectors in gas chromatography. They afford a good compromise in meeting most of the following requirements (4): adequate sensitivity (i.e. large signal to noise ratio), rapid response, applicability to a wide range of compounds with approximately constant sensitivity, linear response with concentration, and insensitivity to flow-rate changes. A further requirement in some analytical procedures is that the separated material should not be destroyed or altered by the detection device. This requirement is met by the gas density balance (5), but not by thermal conductivity cells unless they are operated at low sensing element temperatures, or unless only part of the effluent gas from the column passes through the cell (2), a condition which reduces cell sensitivity.

For analyses such as the determination of trace compounds in gaseous systems, high sensitivity is undoubtedly the most important single requirement. The "sensitivity" of a detector is not always clearly defined in the literature. Dimbat, Porter, and Stross (1) have proposed a "sensitivity parameter" which takes into account recorder sensitivity, chart speed, and carrier gas flow rate, according to the following relationship:

$$S = AC_1C_2C_3 \text{ (ml. mv.)/}w \text{ (mg.)};$$

S = sensitivity parameter,

A = peak area, cm.^2 ,

C_1 = recorder sensitivity, mv. per cm. of chart,

C_2 = reciprocal chart speed, minutes per cm.,

C_3 = flow rate at exit of column, ml. per minute, corrected to column temperature and atmospheric pressure,

w = weight of sample introduced at head of column, mg.

These authors suggest that the noise level (in millivolts) should be given along with the reported sensitivity in describing the performance of a detector. In this connection a distinction should be made between "high frequency" noise (i.e. more than 2 cycles per second) due to vibration of the sensing elements, etc., and base line drift. The latter may be thought of as noise of a very low frequency. Noise of a frequency greater than about 2 cycles per second can usually be eliminated by increasing the time constant of the amplifier circuit without any significant effect on response to the bridge signal.

In the authors' experience the factor limiting the sensitivity of thermal conductivity cells is not the noise level, but the drift of the base line caused at high sensitivities by minute temperature changes in the thermostatted cell and by changes in flow rate. Large-scale drifting, consistently to one side of the base line, may be encountered during

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia.

experiments with rising column temperature when the flow rate changes markedly, or if the pressure differential in the compensating and detecting arms of the cell is altered. The ultimate sensitivity of thermal conductivity cells may depend upon the degree of matching of the filaments or thermistors with regard to electrical properties and geometrical positioning in the channels. In the gas density balance (5) the difficulty in precise matching of detecting and reference columns would be a limiting factor for the sensitivity, especially in experiments with rising column temperature.

The sensitivity of the detectors referred to above appears to be limited by the fact that they measure the change in a physical property of the gas stream caused by the addition of a minute amount of the eluted material. It seemed desirable, therefore, to develop a detector which would be sensitive to the eluted compound only, and would be independent of the relative amount of carrier gas. Differences in ionization potentials were utilized for this purpose. The ionization potential of helium is much greater than that for all other volatile compounds (Table I). The highest ionization potential among the hydrocarbons is that of methane (14.5 volts).

TABLE I
IONIZATION POTENTIALS FOR VARIOUS VOLATILE SUBSTANCES (3)

Substance	Ionization potential (volts)
He	24.5
Ne	21.5
O ₂	12.5
N ₂	15.5
CO ₂	14.4
CH ₄	14.5
CS ₂	10.4
C ₆ H ₆	9.6
C ₆ H ₅ CH ₃	8.5
CH ₂ O	11.3
CH ₃ Br	10.0

EXPERIMENTAL

An ionization gauge (RCA 1949) has been modified to serve as a means of utilizing the relatively low ionization potentials of other compounds in detecting them in a stream of helium (6). The apparatus is shown in Fig. 1. A very small fraction of the gas stream from a standard chromatographic column is diverted through an adjustable leak into the ionization gauge. The potential difference between the filament and grid of the gauge

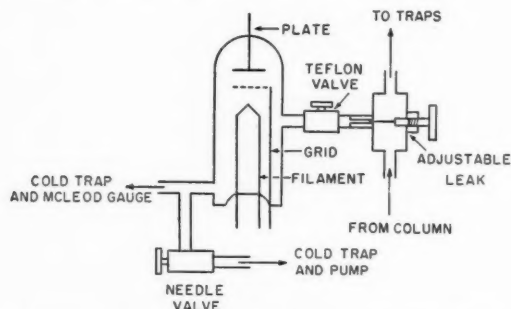


FIG. 1. Schematic diagram showing ionization gauge and adjustable leak.

is adjusted to approximately 18 volts, a value not sufficient to produce ions when helium only is flowing, and consequently there is no plate current. When a substance of lower ionization potential is carried into the gauge, ions are formed. The ion current is amplified in the usual manner and recorded on a Leeds and Northrup Speedomax recorder (sensitivity 1–20 mv. full scale).

For convenience in operation, a metal valve with a Teflon diaphragm was placed between the gauge and the leak. This permits interruption of the gas flow through the gauge without alteration of the setting of the leak. The flow rate and pressure in the gauge could be varied by means of a needle valve located downstream from the gauge. The pressure was measured with a McLeod gauge protected by a dry ice – acetone trap. It was observed that mercury vapor greatly reduced ionization efficiency.

The adjustable leak was made by enlarging the channel of an ordinary Hoke needle valve and drilling a $\frac{5}{16}$ inch hole in the body opposite the tip of the needle. A brass tube, containing a brass plug with a center hole or leak 0.7 mm. in diameter, was soldered into the hole. The "cone" of the original needle was replaced by a sewing needle, the tapered end of which fitted into the leak.

The ionization gauge control unit was a balanced d-c. amplifier with an emission stabilizer. The circuit diagram is given in Fig. 2. Grid and plate potentials for the gauge were supplied by batteries to avoid the use of additional stabilized circuits.

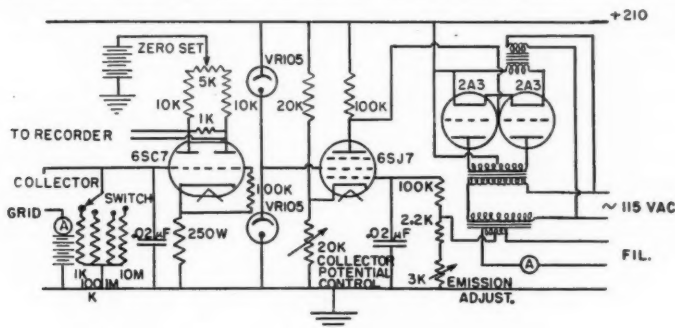


FIG. 2. Circuit diagram of ionization gauge control unit.

Operating Conditions

Over a pressure range in the gauge of from 0.02 to 1.5 mm. of mercury there was a fairly linear relationship between peak height and pressure. The flow rate through the gauge was varied from 13% of the flow through the column (38 ml./minute) to 0.5% at a constant gauge pressure of 0.7 mm. The peak areas were unaffected by the change in flow rate and therefore the ion current seems to depend only on the steady-state pressure in the gauge. At the lower flow rate, tailing of the peaks became noticeable.

The grid potential was found to be the chief factor affecting the sensitivity of the gauge. The variation of peak height with grid potential is shown in Fig. 3 for a typical hydrocarbon. Although the ionization potential of helium is 24.46 volts, grid potentials much less than this value had to be used to avoid ionization of the helium due to the high energy electrons occurring in the Maxwellian distribution with which the electrons leave the filament. The maximum grid potential that could be used was 18 volts. Higher grid potentials might be used at lower filament temperatures where the fraction of high

energy electrons is reduced. The maximum grid potential, and hence the sensitivity, depends also on the purity of the helium. Impurities such as oxygen, nitrogen, and hydrocarbons increase the background ionization in the gauge. The helium was purified before entering the chromatographic system by passing it through a charcoal trap cooled in dry ice - acetone.

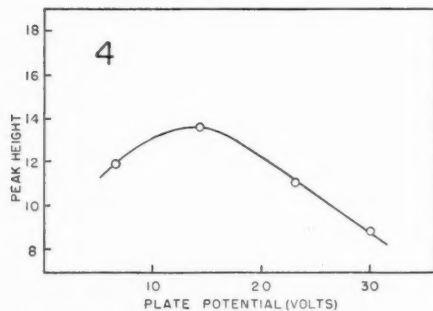
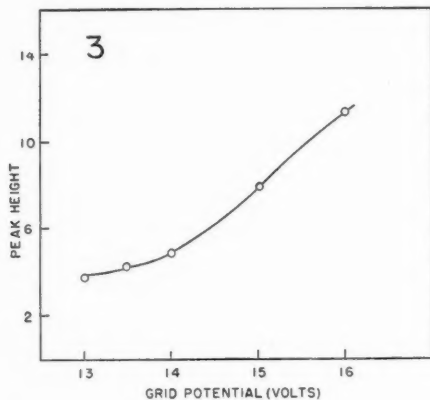


FIG. 3. Variation of peak height with grid potential.

FIG. 4. Variation of peak height with plate potential.

The variation of sensitivity with plate potential is shown in Fig. 4. The observed maximum is presumably due to emission of secondary electrons, penetration of the field into the filament-grid space, and space charge effects.

The sensitivity of the gauge was calculated in terms of the sensitivity parameter (1) on the basis of the following experimental conditions: gauge pressure, 0.7 mm. mercury; filament current, 2.7 ma.; grid potential, +15 volts; collector potential, -15 volts. S for the ionization gauge was found to be 32,500. Values of 312 for a thermistor thermal conductivity cell and 60 for a platinum filament cell operated at low filament temperature have been reported (1, 7). The noise level on the base line was imperceptible under the above operating conditions. The fraction of the effluent gas stream from the column can be reduced to 0.5% without loss of sensitivity or effect on base line stability. The

limit of detection for a typical hydrocarbon was approximately 5×10^{-11} moles (3 mm.^2 peak area).

DISCUSSION

It is anticipated that a further increase in sensitivity may be achieved by operating at higher gauge pressure and by replacing the tungsten filament with an iridium filament, thus minimizing the change in work function that occurs when oxygen and hydrocarbons come in contact with the filament. An additional increase may result from further purification of the helium with consequent increase in base line stability.

The speed of response of the gauge depends chiefly on the velocity with which the eluted compound passes between the electrodes. The cross-sectional area of the gauge as presently constituted is very much greater than that of the main gas stream, but because of the reduction in pressure that occurs on passing through the leak, the flow rate through the gauge is more than 10 times the rate in the main gas stream. Thus only a very small fraction of the effluent gas stream need be used for detection, even though the dead volume of the gauge is large. The volume could be reduced markedly by altering the shape of the envelope and the arrangement of the gauge components.

The gauge is completely insensitive to temperature changes and thus it can be located close to the exit end of the column. This is not desirable with thermal conductivity cells used in experiments with rising column temperature, as the gases must enter the cell at the same temperature as the cell.

At the present stage of development, the ionization gauge detector is useful where it is desired to combine very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature. Its use also eliminates the possibility of pyrolysis of the eluted compounds in the detector after elution from the column. The extent to which sensitivity is related linearly to sample size and is independent of the effect of surface reactions on the filament has not been fully established. It is anticipated that an iridium filament will substantially reduce this latter effect.

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THE REACTION OF ACTIVE NITROGEN WITH HYDROGEN CHLORIDE¹

D. M. WILES² AND C. A. WINKLER

ABSTRACT

Hydrogen chloride was apparently destroyed by catalyzing the recombination of nitrogen atoms, the maximum observed rate of destruction being less than one sixth of the active nitrogen flow rate. The effects on the hydrogen chloride-active nitrogen reaction of added chlorine and added hydrogen indicated the reaction between hydrogen atoms and molecular chlorine to be the most important secondary reaction.

INTRODUCTION

The reactions of active nitrogen with ammonia and with ammonia-ethylene mixtures (2, 9) indicated the possible existence in active nitrogen of a reactive species other than atomic nitrogen, the presence of which appears to be well established (5). Attempts have been made (8, 20) to find other reactions of active nitrogen which could be explained only by assuming a second species to be present, but in both cases an adequate explanation of the results could be given in terms of nitrogen atoms as the only chemically active component.

In the present study the main features of the active nitrogen-hydrogen chloride reaction have been examined to determine whether the presence of a species other than atomic nitrogen must be assumed to explain the results. Only cursory attention has been given to the reaction previously (6, 21). The corresponding reaction between atomic hydrogen and hydrogen chloride, and the effects of added chlorine and added hydrogen on the active nitrogen-hydrogen chloride reaction have also been examined in an effort to determine the degree to which various secondary reactions might affect the rate of decomposition of hydrogen chloride by active nitrogen.

EXPERIMENTAL

The Wood-Bonhoeffer fast-flow system used, and its operation, have been described in an earlier paper from this laboratory (10). The molecular nitrogen flow rate into the discharge tube was 1.15×10^{-4} mole/second and the pressure in the reaction vessel was 1.35 mm. The frequency of the discharge was about 10 per second. An estimate of the active nitrogen flow rate was based on the maximum yield of hydrogen cyanide obtained in the same system from the reaction of active nitrogen with ethylene at high temperatures (12, 18). The experiments with atomic hydrogen were made in the same fast-flow system under conditions which have been described previously (19).

Anhydrous hydrogen chloride, 99% pure, and chlorine, 99.5% pure, were obtained from the Matheson Co., and were purified before use by two vacuum distillations and distillation from a trap at -120° C. Experiments in which the reactant flow rate exceeded 3×10^{-6} mole/second lasted 100 seconds; the others were continued for 300 seconds. The temperature recorded for a given experiment represents the temperature halfway through that experiment, as measured with the thermocouple directly below the reactant inlet in the center of the reaction vessel.

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After each experiment the products and unused reactant were distilled into a small removable trap containing an appropriate absorbing solution, which, in all of the hydrogen chloride work, was 0.2 *N* potassium iodide solution. Flow rates of hydrogen chloride were measured in a series of "blank" experiments during which the nitrogen (or hydrogen) was not activated. The extent of reaction with active nitrogen was found by determining chlorine and unreacted hydrogen chloride simultaneously, using a method similar to that described by Rodebush and Klingelhoefer (16). For the reaction of active nitrogen with mixtures of hydrogen chloride and molecular hydrogen, hydrogen flow rates were calculated from changes in pressure in the known volume of the storage reservoir during the course of the experiments. For the reactions of active nitrogen with hydrogen chloride-molecular chlorine mixtures, chlorine flow rates were measured by determining iodometrically the amounts collected in "blank" experiments.

RESULTS AND DISCUSSION

The reaction between atomic hydrogen and hydrogen chloride was investigated at 50°, 300°, and 440° C. with a wide range of hydrogen chloride flow rates. No net decomposition of hydrogen chloride was detected in any of these experiments but it is reasonable to assume that any decomposition which did occur was nullified by the immediate regeneration of hydrogen chloride in back reactions.

The maximum yield of hydrogen cyanide from the ethylene-active nitrogen reaction was found to be 10^{-5} mole/second at 80° C. and 2×10^{-5} mole/second from 250° to 450° C. An explanation for the dependence of limiting hydrogen cyanide yield on reaction temperature has been proposed (7) which supposes the reactant to act as a third body for the recombination of nitrogen atoms at lower temperatures. On the basis of this reasoning it has been assumed in the present work that the actual flow rate of active nitrogen at all temperatures was 2×10^{-5} mole/second.

The dependence of the rate of hydrogen chloride destruction by active nitrogen on hydrogen chloride flow rate at 80°, 200°, 310°, and 440° C. is shown in Fig. 1. At flow

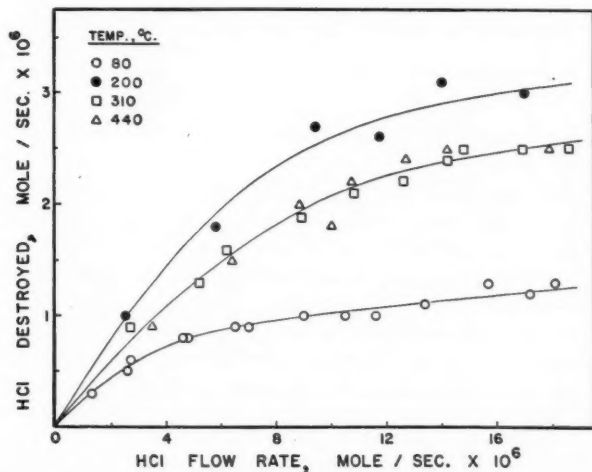


FIG. 1.

rates above 5 or 6×10^{-6} mole/second the characteristic yellow active nitrogen afterglow appeared to be completely replaced by a diffuse and somewhat more reddish reaction flame. Its intensity was visibly greater on the walls and the thermocouple tube than in the body of the gas. The only product recovered was molecular chlorine and it was found that the amount of hydrogen chloride consumed was generally in good agreement with the quantity of chlorine collected.

Fig. 2 shows the changes in the amounts of hydrogen chloride decomposed by active nitrogen at four temperatures when different amounts of molecular chlorine and molecular

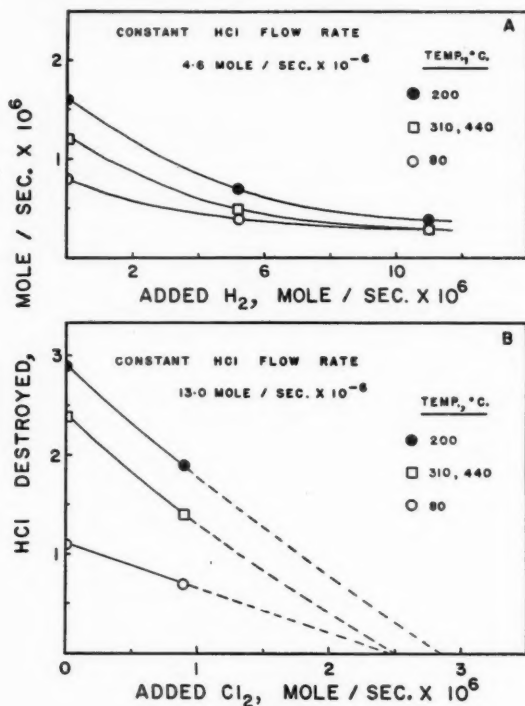
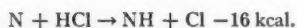


FIG. 2.

hydrogen were added. The effect of adding hydrogen roughly equivalent to hydrogen chloride over a range of flow rates was investigated at the same temperatures, and the results shown in Fig. 3 for 310° and 440° C. are typical.

There is convincing evidence that atomic nitrogen is the main reactive species in active nitrogen (5). A satisfactory explanation of the present results can be given on the basis that atomic nitrogen is the only reactive species. Hence, unlike the results obtained for the ammonia-active nitrogen reaction, the data for the corresponding reaction with hydrogen chloride cannot be considered to support the idea of a second active species.

Although the reaction



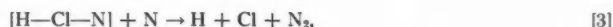
[1]*

*Heats of reaction have been calculated using, for the most part, the heats of formation given in (14). For atomic nitrogen the value 112.5 kcal./mole was used; the value of 77 kcal./mole given by Allshuller (1) for NH has also been used.

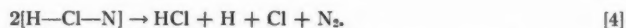
is energetically improbable at ordinary temperatures, sufficient energy for the decomposition of hydrogen chloride would become available by recombination of nitrogen atoms catalyzed by hydrogen chloride. It is suggested that a nitrogen atom and a hydrogen chloride molecule can, on collision, form a relatively stable complex and that when molecular nitrogen is regenerated by collision of this complex with a second nitrogen atom (or with a second complex) a sufficient proportion of the recombination energy (9.76 ev. per mole) is left in the H—Cl bond to cause decomposition of the molecule. The decomposition of hydrogen chloride by active nitrogen would then be represented by



followed either by

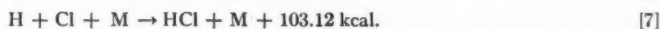
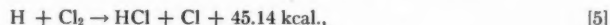


or by



There is no direct experimental evidence for a nitrogen atom - hydrogen chloride complex but, by analogy with the H—Cl—H complex (11, 17), it may be predicted (4) that the atomic nitrogen complex should form relatively readily and should have a reasonable lifetime.

Any mechanism which is postulated to explain the results shown in Fig. 1 must account for the facts that increasing the temperature above 200° C. lowers the rate of hydrogen chloride consumption, that the rates at 310° and 440° C. are the same, within experimental error, and that none of the three curves seems to have levelled off at a plateau value, within the range of flow rates used. These facts indicate that one or more back reactions affect the observed rates by regenerating hydrogen chloride. The only possible back reactions are:



The activation energies for reactions [5] and [6] have been reported as 3 and 6 kcal. per mole, respectively (13). Hydrogen atoms, besides taking part in reactions [5] and [7], can recombine to form molecular hydrogen or can decompose hydrogen chloride in the reaction



which probably has an activation energy of about 5 kcal. per mole (13). Chlorine atoms can either combine to form molecules or react in [6] or [7].

It is important to determine, if possible, which of the above processes are more important at any given temperature. It is evident from Figs. 2A and 3 that additions of molecular hydrogen affect the observed rate of hydrogen chloride decomposition much less than do additions of chlorine. This observation is in accord with the suggestion (15) that k_5/k_6 is at least 100, up to 25° C. Morris and Pease (13) estimate that k_5/k_6 is greater than 100 at room temperature; Fig. 2B indicates that even at temperatures up to 440° C. with excess hydrogen chloride, hydrogen atoms react in process [5] to a much greater extent than in [8]. The amount of hydrogen chloride produced in reaction [7] is probably small at all the temperatures owing to the infrequency of triple collisions in the gas phase and the number of rapid alternative processes possible for atomic hydrogen and atomic chlorine before they reach the vessel wall.

It seems reasonable to conclude that: (i) reaction [5] is the most important back

reaction at all temperatures at which the reactions were studied; (ii) reaction [8] occurs to a somewhat greater extent than reaction [6], particularly at higher hydrogen chloride flow rates, because there probably are more hydrogen atoms than molecules in the system; (iii) most of the hydrogen atoms produced in reactions [3] and [4] react before they recombine, whereas chlorine atoms, produced in the same reactions, recombine to a large extent (the conditions that favor recombination of chlorine atoms differ from those that favor recombination of hydrogen atoms (16)); (iv) recombination of hydrogen

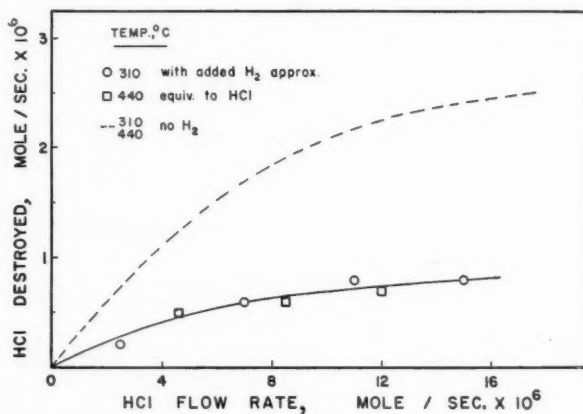


FIG. 3.

atoms, which is certain to occur to some extent, is the main factor preventing the complete regeneration of hydrogen chloride, i.e., for permitting the decomposition of hydrogen chloride by active nitrogen to be observed at all.

To explain the comparable rates of hydrogen chloride consumption observed at 310° and 440° C. it must be assumed that changes in the extent of reactions [2], [3], [4], and [8] are just balanced by changes in the amount of hydrogen chloride regenerated by [5], [6], and [7]. This situation seems entirely too coincidental unless it is assumed that there is complete consumption of nitrogen atoms at or below 310° C. (i.e. 10^{-5} mole/second hydrogen chloride destroyed with the nitrogen atom flow rate 2×10^{-5} mole/second). On the basis of this assumption it can be shown that changes in the extent of the secondary reactions between 310° and 440° C. are likely to be within experimental error. Extrapolation of the data of Bodenstein *et al.* (3) indicates that the ratio k_5/k_8 does not change appreciably between 310° and 440° C. in a flow system. The fact that added chlorine and added hydrogen had the same effects (Fig. 2) at 310° C. as they had at 440° C. indicates that the extent of reactions [5], [6], [7], and [8] does not change significantly in this interval.

The decrease in rate of hydrogen chloride consumption (see Fig. 1) as the temperature is increased from 200° to 310° C. and above may be attributed to an increase in the rates of the reactions that regenerate hydrogen chloride, particularly reaction [5] and perhaps, to a lesser extent, reaction [6]. However, this decrease also implies that there is little or no increase in the initial extent of the destruction of hydrogen chloride by nitrogen atoms between 200° and 300° C., i.e., that it is approximately 10^{-5} mole/second over the whole range 200° to 440° C.

The increase in the rate of decomposition of hydrogen chloride as the temperature is increased from 80° to 200° C. can be attributed to an increase in the rate of the primary decomposition by nitrogen atoms, or to an increase in the rate of reaction [8], or possibly to a combination of the two. However, at the flow rates used in this work, it is probable that most of the observed increase in the rate of hydrogen chloride decomposition is due to an increase in the rate of reactions [2], [3], and [4]. This would imply a small temperature coefficient associated with one or more of these reactions.

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REDUCTION OF HALOGENATED NITROBENZENES¹

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ABSTRACT

2-Chloronitrobenzene and 2,5-dichloronitrobenzene were reduced with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol. The effects of sodium hydroxide, temperature, time, Tergitol, and Lignosol were studied for the arsenite and dextrose reductions. 2-Bromonitrobenzene was also reduced with sodium arsenite and dextrose in alkaline medium. These reductions gave rise to four new phenazine derivatives. 2,4-Dinitrochlorobenzene, when reduced with sodium arsenite, in alkaline medium, yielded only 2,2'-dichloro-5,5'-dinitroazoxybenzene.

INTRODUCTION

In 1841, Zinin (14) prepared azoxybenzene for the first time by reducing nitrobenzene and showed that the compound was an intermediate product in the formation of aniline. Since that time many other interesting and useful substances have been obtained from nitrobenzene, for instance, nitrosobenzene, phenylhydroxylamine, azobenzene, and hydrazobenzene.

A great variety of reagents have been used effectively to reduce nitrobenzenes. With an alkaline medium the formation of azoxy compounds was favored. Reduction with sodium and potassium methoxides and ethoxides proved to be efficient. Klinger and Pitschke (9) reduced *m*-dinitrobenzene to *m*-dinitroazoxybenzene with sodium methoxide and similarly Lachmann prepared azoxybenzene from nitrobenzene. Other reagents such as sodium amalgam and alcohol, stannous chloride, ferrous sulphate, and zinc dust in alkaline media have been extensively used. Elbs (5) electrolyzed nitrobenzene in a strong sodium hydroxide solution and obtained hydrazobenzene as the main product.

Flürscheim and Simon (6) reduced 3,5-dichloro-4-bromonitrobenzene to the azoxy compound in quantitative yield with stannous chloride in acid medium, but in general an alkaline medium is best to prepare azoxy compounds.

In 1928, Zechmeister and Rom (13) reduced 3-bromonitrobenzene with zinc dust in alcoholic saturated ammonium chloride solution and obtained 3,3'-dibromoazoxybenzene.

Sodium arsenite has been used to a limited extent so far for nitro compounds, for instance, Loesner (11) prepared azoxybenzene from nitrobenzene with this reagent in strong alkaline solution. Bigelow and Steeves (2) have successfully obtained azoxy derivatives by using sodium arsenite. In 1949, Gaudry and Keirstead (7) reduced seven chloronitrobenzenes to azoxybenzenes with alkaline solutions of dextrose and sodium arsenite.

The object of the present work was to investigate the reduction of halogenated nitrobenzenes with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol.

THEORETICAL PART

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

In order to identify all the products formed, the reduction of 2-chloronitrobenzene with

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TABLE I
REDUCTION OF HALOGENATED NITROBENZENES WITH SODIUM ARSENITE

Compound	Amount, moles	As ₂ O ₃ , moles	NaOH, moles	H ₂ O, ml.	CH ₃ OH, ml.	Time, hr.	Temp., °C.	Starting material			Yield, %		
								Azoxy	Amine	Phenazines			
2-Chloronitrobenzene	0.32	0.25	2.00	300	130	3	80	15	39	C ₁₂ H ₉ O ₂ N ₂ Cl, 1.8			
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	85	14	36	C ₁₂ H ₉ O ₂ N ₂ Cl, 2.1			
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	12	80	11	39	C ₁₂ H ₉ O ₂ N ₂ Cl, 1.8			
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	80	18	22	Traces			
2-Chloronitrobenzene	1.91	1.52	10.50	1800	780	1	88	29	26	C ₁₂ H ₉ O ₂ N ₂ Cl, 5.0			
2,5-Dichloronitrobenzene	0.33	0.28	1.62	300	130	2	81	19	37	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 2.7			
2,5-Dichloronitrobenzene	0.78	0.76	5.25	900	390	2	85	1	78	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 0.1			
2-Bromonitrobenzene	0.27	0.25	1.75	300	130	3	82	28	13	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 3.2			
2,4-Dinitrochlorobenzene	0.33	0.25	1.75	250	130	2	82	1	3	Traces			
										C ₁₂ H ₇ O ₂ N ₂ Br, 1.0			
										Nil			

TABLE II
REDUCTION OF HALOGENATED NITROBENZENES WITH DEXTROSE

Compound	Amount, moles	Dextrose, moles	NaOH, moles	H ₂ O, ml.	CH ₃ OH, ml.	Time, hr.	Temp., °C.	Starting material			Yield, %		
								Azoxy	Amine	Phenazines			
2-Chloronitrobenzene	0.17	0.13	0.76	270	—	1	80	7	78	C ₁₂ H ₉ O ₂ N ₂ Cl, 2.0			
2-Chloronitrobenzene	0.17	0.13	0.75	230	80	3	80	32	45	C ₁₂ H ₉ O ₂ N ₂ Cl, 0.5			
2-Chloronitrobenzene	0.17	0.13	0.75	70	—	1	60	Nil	96	Nil			
2-Chloronitrobenzene	1.00	0.75	10.50	1500	480	1	88	55	21	C ₁₂ H ₉ O ₂ N ₂ Cl ₂ , 1.8			
2,5-Dichloronitrobenzene	0.17	0.13	0.75	400	—	1	80	4	78	Traces			
2,5-Dichloronitrobenzene	0.17	0.13	0.75	225	—	1	70	18	88	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 1.3			
2-Bromonitrobenzene	0.06	0.05	0.27	90	30	2	86	5	19	C ₁₂ H ₇ O ₂ N ₂ Br, 1.9			
										C ₁₂ H ₉ O ₂ N ₂ Br, 1.7			

sodium arsenite in alkaline medium was carried out by means of an efficient procedure described in the experimental part. The purple substance obtained, chlorotrihydroxydihydrophenazine, was shown to be a phenazine derivative by degradation and its structure will be discussed in a forthcoming publication.

Many experiments were carried out to increase the yields, a few of which are mentioned in Table I. The effects of the concentration of sodium hydroxide, temperature, and time were thoroughly investigated.

The formation of 2,2'-dichloroazoxybenzene and of chlorotrihydroxydihydrophenazine was shown to be dependent upon the concentration of sodium hydroxide. The yield of 2-chloroaniline was not greatly influenced. Variation of the temperature had a profound effect on the reaction. The optimum temperature for the formation of the azoxy compound was found to be 85° C. and for the highest yield of chlorotrihydroxydihydrophenazine, 80° C. Lower temperature favored the formation of the amine. The refluxing time was an important factor, but the reduction was not influenced by the rate of stirring.

It was thought of interest to determine the effect of dispersing agents. Tergitol-08 (4) was used in an attempt to facilitate the reaction taking place. The yield of the azoxy compound was increased but that of chlorotrihydroxydihydrophenazine was decreased. It appears that better mixing of the reactants due to Tergitol-08 favors the formation of the azoxy compound rather than that of the phenazine. Lignosol (1) was also used but this was not simply a dispersing agent for it is known to contain the reducing sugar glucose. The effect of Lignosol was similar to that of Tergitol-08.

In order to prepare chlorotrihydroxydihydrophenazine in sufficient quantities, several large scale reductions were carried out. With large quantities the yield of chlorotrihydroxydihydrophenazine was raised to 5.0% as indicated in Table I.

The yield of chlorotrihydroxydihydrophenazine from the sodium arsenite reduction of 2-chloronitrobenzene was originally so small that it was possible that the compound was formed only from impurities present in the practical starting material. To verify that this was not the case, 2-chloronitrobenzene which had been purified by steam distillation was used. Chlorotrihydroxydihydrophenazine was still isolated but in lower yield. This showed that impurities, like 4-chloronitrobenzene for instance, influenced the formation of the phenazine.

Accordingly, various substances, for instance 2-nitrophenol, 4-nitrophenol, and 2-chloroaniline, were added in a series of reductions. Both 2-nitrophenol and 2-chloroaniline increased the yield of chlorotrihydroxydihydrophenazine but 4-nitrophenol did not.

The effect of the solvent on the reduction was investigated. When no alcohol was present there was no formation of the phenazine or amine and the yield of the azoxy compound was low. Methanol and ethanol increased the yield of chlorotrihydroxydihydrophenazine. With isopropanol, the yields of all the products were very low. The solvent is very important and determines the course of the reduction, as shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

Dextrose in alkaline medium has had limited use as a reducing agent for nitrobenzenes. Noetling (12) prepared azoxybenzene and Lacy and Brouillard (10) obtained 2,2'-dichloroazoxybenzene. In 1951, Galbraith, Degering, and Hitch (8) used dextrose and sodium hydroxide to reduce a few aromatic nitro compounds.

TABLE III
 EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2-CHLORONITROBENZENE

Water, ml.	Alcohol, ml.	Temp., ° C.	Yield, %			
			$C_6H_4O_2NCl$	Azoxy	Amine	$C_{12}H_9O_3N_2Cl$
300	No alcohol	107	50	5	Nil	Nil
300	Methanol, 130	80	5	23	0.5	8.1
130	Methanol, 250	80	10	35	Traces	8.9
300	Ethanol, 130	85	16	28	1.0	13.9
180	Ethanol, 250	82	28	7	Nil	5.1
180	Isopropanol, 250	87	48	5	0.2	0.1

In the present work, the reduction of 2-chloronitrobenzene with dextrose in alkaline medium was further studied. A few of the results obtained are given in Table II. The effects of the concentration of sodium hydroxide and time were investigated separately. The concentration of sodium hydroxide was found to be of importance. The refluxing time greatly influenced the reduction; the yield of the azoxy compound was increased when the period of refluxing was lengthened but that of chlorotrihydroxydihydrophenazine was decreased.

Several factors were varied simultaneously: refluxing time, temperature, and methanol and water contents. The yield of 2,2'-dichloroazoxybenzene was increased to 96%. A low temperature for the first hour followed by higher temperature for the remainder of the refluxing period was particularly favorable for azoxy formation. When ethanol instead of methanol was used as a solvent, the yields of the amine and azoxy compounds were decreased, but that of chlorotrihydroxydihydrophenazine was increased.

In general, the yield of 2,2'-dichloroazoxybenzene was much higher when dextrose was used instead of sodium arsenite. It was the opposite for chlorotrihydroxydihydrophenazine, the yield being lower. Both methods gave low yields of amine as expected with mild reducing agents.

Reduction of 2-Chloronitrobenzene with Lactose

In view of the successful use of dextrose as a reducing agent for nitrobenzenes, it was of interest to try other reducing sugars for this purpose. 2-Chloronitrobenzene was reduced for the first time with lactose in alkaline medium; 2,2'-dichloroazoxybenzene and 2-chloroaniline were isolated together with chlorotrihydroxydihydrophenazine. An important feature of the reduction with lactose was that tar formation was negligible, greatly facilitating the extraction of the azoxy compound.

Reduction of 2-Chloronitrobenzene with Maltose

Maltose was also used to reduce 2-chloronitrobenzene and the results were similar to those obtained with lactose.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

It was thought that the alcohol present in the reaction mixture was not merely acting as a solvent and this idea was supported by the fact that replacing methanol by ethanol led to increased yields of chlorotrihydroxydihydrophenazine. In order to see if there was any reaction, 2-chloronitrobenzene was heated with sodium hydroxide and alcohols. With ethanol, 2,2'-dichloroazoxybenzene and chlorotrihydroxydihydrophenazine were formed but no amine. With methanol, the only product isolated was 2-chloroaniline.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

When 2-chloronitrobenzene was treated with potassium hydroxide and ethanol, there

was no formation of a phenazine. The main product of the reduction was 2,2'-dichloroazobenzene. 2,2'-Dichloroazoxybenzene and 2-chloroaniline were also formed.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene was reduced with sodium arsenite in alkaline medium. Two new compounds were obtained and shown to be phenazine derivatives by degradation to phenazine. An efficient procedure was developed to isolate them completely together with the other products: 2,5-dichloroaniline, 2,2',5,5'-tetrachloroazoxybenzene, sodium arsenate, and sodium carbonate.

In order to prepare the new phenazines in sufficient quantities, many reductions were carried out and two are mentioned in Table I. The effect of alcohols was studied. Experiments were performed in the absence of alcohol and in the presence of methanol, ethanol, and isopropanol. With no alcohol present, 2,5-dichloroaniline was formed in good yield. With methanol, the yield of the azoxy compound was raised. With ethanol, the yields of trichlorotrihydroxydihydrophenazine and trichlorodihydroxydihydrophenazine were increased. As expected, with isopropanol the yield of trichlorotrihydroxydihydrophenazine was low and no trichlorodihydroxydihydrophenazine was isolated, but 2,5-dichloroaniline was obtained in high yield. The results are given in Table IV.

TABLE IV
EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2,5-DICHLORONITROBENZENE

Alcohol, ml.	Temp., °C.	Yield, %				
		$C_6H_3O_2NCl_2$	Azoxy	Amine	$C_{12}H_7O_3N_2Cl_3$	$C_{12}H_7O_2N_2Cl_3$
No alcohol	91	23	41.6	14.0	2.3	0.4
Methanol, 130	82	Nil	73.0	0.6	6.2	1.0
Methanol, 250	79	Nil	64.0	1.0	6.6	1.1
Ethanol, 130	86	6	64.0	7.0	14.0	1.9
Ethanol, 250	83	6	42.3	11.0	3.5	0.8
Isopropanol, 130	86	25	43.9	12.0	2.3	Nil

Reduction of 2,5-Dichloronitrobenzene with Dextrose

The reduction of 2,5-dichloronitrobenzene with dextrose in alkaline medium was studied. Two experiments are mentioned in Table II.

The reaction was found to be dependent upon the concentration of sodium hydroxide and the temperature. Tergitol-08 was added in a series of reductions and the yield of the azoxy compound was increased to 85%. Reduction with dextrose in the presence of ethanol gave higher yields of 2,5-dichloroaniline and trichlorotrihydroxydihydrophenazine, but no trichlorodihydroxydihydrophenazine was isolated.

Reduction of 2,5-Dichloronitrobenzene with Lactose

Lactose in alkaline medium was employed to reduce 2,5-dichloronitrobenzene and the main product was 2,2',5,5'-tetrachloroazoxybenzene. 2,5-Dichloroaniline was also isolated together with the trichlorohydroxydihydrophenazines. Tar formation was negligible. The details are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was also treated with maltose in alkaline medium. The results were similar to those obtained with lactose and are shown in Table V.

It appears that these reducing sugars are ideal for the reduction of nitrobenzenes to

TABLE V
REDUCTIONS OF 2,5-DICHLORONITROBENZENE WITH OTHER REDUCING AGENTS

Compound	Amount, moles	Reducing agent	NaOH, moles	H ₂ O, ml.	Alcohol, ml.	Time, Temp., hr. °C.	Starting material	Yield, %	
								Azoxy Amine	Phenazines
2,5-Dichloronitrobenzene	0.17	Lactose, 0.17	0.75	300	Methanol, 100	2	88	5 36	1.1 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , 0.9 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , 0.3 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , 1.0 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , 0.4
2,5-Dichloronitrobenzene	0.17	Maltose, 0.17	0.75	270	Methanol, 100	2½	88	14 34	0.5 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil
2,5-Dichloronitrobenzene	0.32	—	1.75	300	Methanol, 130	2	85	79 2	0.8 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil
2,5-Dichloronitrobenzene	0.32	—	1.75	160	Methanol, 250	2	83	82 7	0.5 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil
2,5-Dichloronitrobenzene	0.32	—	1.75	300	Ethanol, 130	2	84	12 13.0	2.8 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , 3.0 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil
2,5-Dichloronitrobenzene	0.32	—	1.75	180	Ethanol, 250	2	82	10 37	11.5 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil
2,5-Dichloronitrobenzene	0.06	KOH, 0.38	—	—	Ethanol, 100	2	85	1 Nil*	23.4 C ₁₂ H ₇ O ₂ N ₂ Cl ₃ , Nil

*2,2',5,5'-Tetrachloroazobenzene was obtained. Yield, 9%.

TABLE VI
PHENAZINES FROM REDUCTIONS OF HALOGENATED NITROBENZENES

Compound	M.p., ° C.	Formula	Color	Analysis							
				Calculated, %			Found, %				
				C	H	N	Halogen	C	H	N	Halogen
Chlorotrihydroxydihydrophenazine	156	C ₁₂ H ₇ O ₂ N ₂ Cl	Purple	54.45	2.43	10.59	13.40	54.25	3.47	10.40	13.65
Trichlorotrihydroxydihydrophenazine	127-128	C ₁₂ H ₄ O ₂ N ₂ Cl ₃	Red	43.20	2.12	8.39	31.89	43.10	2.30	8.50	32.17
Trichlorotrihydroxydihydrophenazine	154	C ₁₂ H ₄ O ₂ N ₂ Cl ₃	Yellow	45.38	2.23	8.82	33.49	45.20	2.39	8.98	33.81
Bromotrihydroxydihydrophenazine	167-168	C ₁₂ H ₆ O ₂ N ₂ Br	Red	46.62	2.93	9.06	25.85	46.84	3.04	9.33	25.71

azoxy compounds. The use of other agents like alcoholic potassium hydroxide and sodium alcoholate in alcoholic solution was limited by such factors as low yields, impure products, or violent reactions.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

In view of the increased yields of the phenazines when the reduction was performed in the presence of ethanol, it was thought of value to determine if this effect was due to some reducing action of ethanol in alkaline medium. Thus 2,5-dichloronitrobenzene was heated with sodium hydroxide and alcohols. With methanol, small amounts of the amine and azoxy compound were formed, but no phenazines were isolated, as shown in Table V. With ethanol, 2,2',5,5'-tetrachloroazoxybenzene and 2,5-dichloroaniline were obtained in higher yields. Trichlorotrihydroxydihydrophenazine was isolated but no trichlorodihydroxydihydrophenazine. This result showed that the alcohol did not merely act as a solvent.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol in an attempt to prepare the new chlorohydroxydihydrophenazines. The main product of the reaction was 2,5-dichloroaniline, as mentioned in Table V. Interesting features were that no azoxy compound or phenazines were isolated, but 2,2',5,5'-tetrachloroazobenzene was formed.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—Zechmeister and Rom (13) reduced 2-bromonitrobenzene with magnesium and methanol and obtained 2,2'-dibromoazoxybenzene. In the present work, 2-bromonitrobenzene was reduced with sodium arsenite in alkaline medium. The main product was 2,2'-dibromoazoxybenzene, and the others were 2-bromoaniline and a bromotrihydroxydihydrophenazine, as shown in Table I.

Reduction with dextrose.—Reduction of 2-bromonitrobenzene with dextrose in alkaline medium gave similar results, indicated in Table II, but the yields of the products were higher.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

In 1914, Brand and Eisenmenger (3) reported the formation of a dichlorodinitroazoxybenzene by the electroreduction of 2,4-dinitrochlorobenzene. In the present work, 2,4-dinitrochlorobenzene was reduced with sodium arsenite in alkaline medium and 2,2'-dichloro-5,5'-dinitroazoxybenzene was isolated, as mentioned in Table I. This compound had the same melting point, 163–164° C., as that given by Brand and Eisenmenger for their product. However, no amine or phenazine compounds were detected in the preparation.

EXPERIMENTAL PART*

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

A sodium arsenite solution was prepared by treating arsenic trioxide (50.0 g., 0.25 mole) with water (50 ml.). The mixture was stirred until a thick white paste was formed. Sodium hydroxide (70.0 g., 1.75 moles) was cautiously added together with water (250 ml.) in small portions. Heat was evolved and gradually the solution became colorless.

Several attempts were made to reduce 2-chloronitrobenzene by sodium arsenite which had not been freshly prepared from arsenic trioxide and sodium hydroxide. No reaction

*All melting points are uncorrected.

occurred. Therefore, to reduce 2-chloronitrobenzene, it is absolutely necessary to use freshly prepared sodium arsenite.

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in methanol (130 ml.) and the solution was placed in a 1-liter three-necked flask. The flask was fitted with a powerful stirrer, thermometer, and a small reflux condenser. The freshly prepared solution (300 ml.) of sodium arsenite was added through the side neck of the flask and the temperature was raised to 80° C. by means of a heating jacket. This temperature was maintained for 3 hours, the contents of the flask being refluxed vigorously all the time. In the first stage of the reduction the color was yellow and it gradually changed to orange, then red, and finally purple.

After being refluxed, the contents of the flask were separated, as indicated in Fig. 1, by steam distillation into two parts: mixture I, which remained in the reaction flask, and

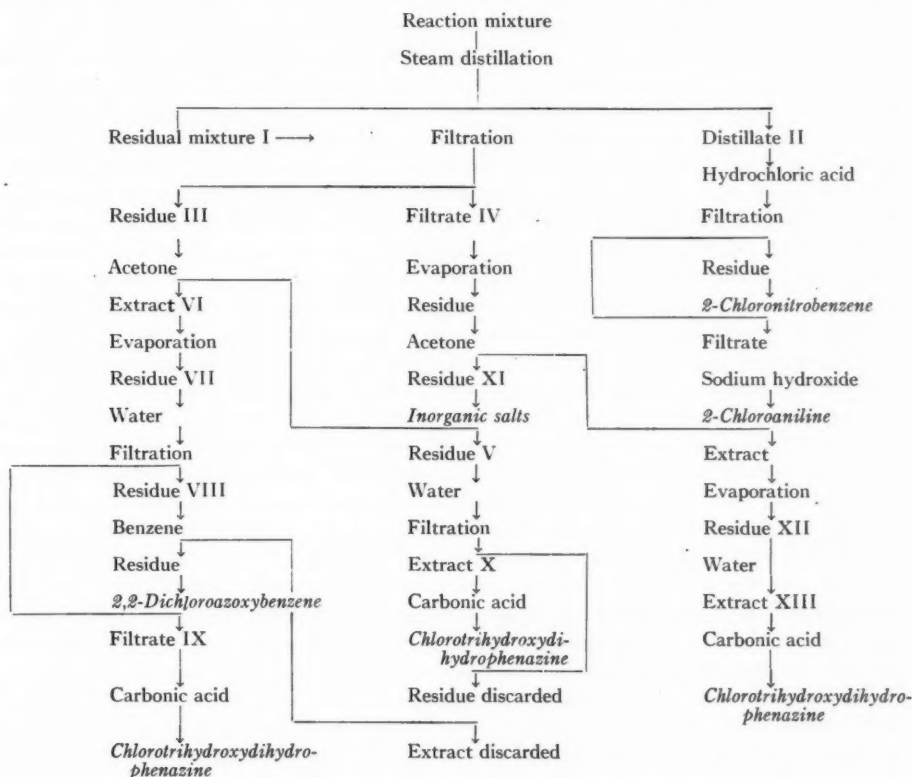


FIG. 1. Reduction of 2-chloronitrobenzene with sodium arsenite.

a distillate, II. The distillate, II, was acidified with hydrochloric acid and filtered to separate the pale yellow plates of 2-chloronitrobenzene, m.p. 32.5° C. Yield, 5%. The filtrate was made alkaline with sodium hydroxide and extracted with ether. The ethereal extract was evaporated to dryness and the residue was converted into the acetyl derivative of 2-chloroaniline. The yield of 2-chloroaniline was 0.5%.

The mixture, I, remaining in the reaction flask after steam distillation was filtered; a residue, III, and a deep red filtrate, IV, were obtained. Residue III was extracted with acetone, giving a residue, V, and a deep red colored extract, VI.

The acetone extract, VI, was evaporated to dryness. The black residue, VII, thus obtained was first extracted with a large volume of boiling water to give a residue, VIII, and a deep red filtrate, IX, which was treated with carbon dioxide to produce a red precipitate of chlorotrihydroxydihydrophenazine, recrystallized from ethanol as purple needles, m.p. 156° C. Yield, 0.5%. This product was shown to be a phenazine derivative by degradation. A small quantity was ground with zinc dust and the mixture poured into a pyrex test tube and covered with an equal volume of zinc dust. The zinc dust was heated gently first and the mixture of zinc dust and the compound was heated later to a dull red heat. A pale yellow product was obtained as a sublimate on the cooler part of the test tube. It was recrystallized from petroleum ether as yellow needles, m.p. 171° C. alone or with an authentic sample of phenazine.

The residue VIII was treated several times with cold ethanol to remove tars. Further treatments with benzene and charcoal yielded almost pure 2,2'-dichloroazoxybenzene which was recrystallized from a mixture of benzene and ethanol, as light yellow needles, m.p. 56° C. alone or with an authentic sample. Yield, 23%. An alternative procedure for obtaining crude 2,2'-dichloroazoxybenzene from the acetone extract VI was to precipitate the crude material with water and recrystallize from aqueous ethanol.

The residue V from steam distillation, which was insoluble in acetone, was extracted with copious volumes of boiling water. The portion insoluble in water (0.1 g.) was discarded and the red aqueous solution, X, upon treatment with carbon dioxide, yielded a red precipitate. Several recrystallizations from ethanol or glacial acetic acid gave purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. Yield, 3.8%.

The deep red liquid, IV, from the reaction flask, after steam distillation, was evaporated to dryness. A purple-gray mass was obtained. Extraction with acetone gave a grayish-white residue, XI, and a red colored solution. A purple residue, XII, was obtained upon removal of the solvent and was extracted with large volumes of boiling water. Treatment of the extract, XIII, with carbon dioxide gave a red product which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 155–156° C. Yield, 1.3%. The grayish-white residue, XI (132 g.), insoluble in acetone, was treated with the following solvents: benzene, ether, methanol, ethanol, and petroleum ether. It was insoluble in all these solvents, but soluble in water; a portion of the residue dissolved in water was tested for arsenate using copper sulphate solution. A blue precipitate was obtained, indicating the presence of arsenate. A small amount, when heated on a platinum wire, gave a positive test for sodium.

The chlorotrihydroxydihydrophenazine prepared was very soluble in glacial acetic acid, soluble in benzene, ether, carbon tetrachloride, pyridine, and aniline, fairly soluble in acetone and ethanol, slightly soluble in methanol and petroleum ether, and insoluble in water. The total yield of chlorotrihydroxydihydrophenazine was 5.5%. The analysis is given in Table VI, and the structure will be discussed in a forthcoming publication.

Reduction on a larger scale.—Several reductions were carried out on a larger scale. The details of the experiment which gave the best yield of chlorotrihydroxydihydrophenazine, 5.0%, are given in Table I.

Effect of sodium hydroxide.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with sodium arsenite solutions containing arsenic trioxide

(50.0 g., 0.25 mole), water (300 ml.), and various quantities of sodium hydroxide (1.25–2.00 moles). The reaction mixture was refluxed for 3 hours at 80° C.

The optimum amount of sodium hydroxide for the best yield of the phenazine derivative (3.8%) was 1.75 moles and for that of the azoxy compound (39%) was 2.00 moles, as indicated in Table I.

Effect of temperature.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with a sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole), water (300 ml.), and sodium hydroxide (70.0 g., 1.75 mole). The mixture was refluxed for 3 hours in all the experiments and the temperature was varied from 70° to 85° C.

The temperature could not be varied over a wide range, because the highest temperature possible was that of the boiling point of the solution and the lowest was 70° C., the temperature needed to prevent solidification of the reaction mixture.

The optimum temperature for the best yield of the azoxy compound (36%) was 85° C. and for that of the phenazine derivative (3.8%) was 80° C., as shown in Table I.

Effect of time.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced in the same way as described above using a temperature of 80° C., but the reaction time was varied from 1 to 48 hours.

The optimum refluxing time for the best yield of the azoxy compound (39%) was 12 hours, and for that of the phenazine derivative (3.8%) was 3 hours, as shown in Table I.

Effect of Tergitol-08.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced again under the same conditions as previously mentioned, in the presence of different quantities (0.25 to 1.00 ml.) of Tergitol-08. Tergitol-08 (0.5 ml.) increased the yield of the azoxy compound by 10%.

Effect of Lignosol.—In another series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) varying amounts (0.25 to 5.00 g.) of Lignosol were added. The use of Lignosol (5.00 g.) increased the yield of the azoxy compound by 8%.

Effect of purity of starting material.—In order to show that the chlorotrihydroxydihydrophenazine formed during the reduction of 2-chloronitrobenzene was not due to impurities in the starting material, reductions were carried out using purified material. The phenazine was still isolated.

Effect of addition of substances.—2-Nitrophenol, 4-nitrophenol, and 2-chloroaniline were added in a series of reductions of 2-chloronitrobenzene. Only 2-nitrophenol and 2-chloroaniline increased the yield of the phenazine.

Effect of alcohols.—A series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) was carried out using arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70.0 g., 1.75 mole) in the presence of alcohols. The reaction mixtures were refluxed for 3 hours. The results are shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.) and the solution placed in a 1-liter three-necked flask fitted with an efficient stirrer, thermometer, and reflux condenser. Sodium hydroxide (30.0 g., 0.75 mole) and water (250 ml.) were added and the reaction mixture heated to 60° C. At that temperature a thick sirup of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was slowly added. The mixture was refluxed at 88–89° C. for 40 minutes. The reaction mixture was steam distilled until no more viscous droplets appeared in the steam distillate, which was later treated with hydrochloric acid and filtered. The residue was recovered 2-chloronitrobenzene, m.p. 33° C. Yield, 38%.

The acid distillate was made alkaline with sodium hydroxide and extracted with ether. Removal of the ether from the extract gave a residue, which was converted to the acetyl derivative of 2-chloroaniline, m.p. 87–88° C. The yield of 2-chloroaniline was 1.9%. The solution from steam distillation was filtered, and the filtrate discarded. A black residue was obtained, which was extracted with acetone, the acetone extract evaporated to dryness, and the residue, 2,2'-dichloroazoxybenzene, recrystallized from ethanol, m.p. 56° C. alone or with an authentic sample. Yield, 35%. The portion of the residue not soluble in acetone was extracted with large volumes of hot water, and the extract treated with carbon dioxide. A red flocculent precipitate was obtained, which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. Yield, 1.4%. Calculated for $C_{12}H_9O_3N_2Cl$: C, 54.45%; H, 3.43%; N, 10.59%; Cl, 13.40%. Found: C, 54.30%; H, 3.55%; N, 10.53%; Cl, 13.67%.

Reduction on a larger scale.—2-Chloronitrobenzene was reduced on a larger scale and the experimental details are given in Table II.

Effect of sodium hydroxide.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was carried out, using a paste of dextrose (23.0 g., 0.13 mole) in water (15 ml.), added in portions. The concentration of sodium hydroxide present was varied by using different amounts of water (70 to 370 ml.) in the reaction mixtures. The reaction mixtures were refluxed at 80° C. for 30 minutes. The same extraction procedure as previously described was used. A 10% solution was the optimum for the best yield of the azoxy compound (78%) and also for the phenazine derivative (2.0%).

Effect of time.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was performed, using a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole), water (230 ml.), and methanol (80 ml.). The reaction mixtures were refluxed at 80° C. for varying times (10 to 180 minutes). With a refluxing time of 3 hours the yield of the azoxy compound was raised to 45% from 23% obtained after 10 minutes refluxing.

Effect of time, temperature, methanol, and water.—The same procedure as in the previous series was used but time, temperature, methanol, and water contents were varied. The dextrose paste was added in portions. The yield of the azoxy compound was raised to 96%; the reaction conditions are shown in Table III.

Effect of ethanol.—2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in ethanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (230 ml.) were added. The reaction mixture was heated to 60° C. and a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was added slowly. The mixture was refluxed at 86–87° C. for 2 hours. Steam distillation was followed by the usual extraction treatment and the products were isolated. Unreacted 2-chloronitrobenzene (yield, 9%) was recovered. A trace of 2-chloroaniline was formed. 2,2'-Dichloroazoxybenzene (yield, 20%) and chlorotrihydroxydihydrophenazine (yield, 4.4%) were obtained.

Reduction of 2-Chloronitrobenzene with Lactose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 50° C. and a thick paste of lactose (46.1 g., 0.17 mole) in water (30 ml.) was added.

The reaction mixture was refluxed at 87–88° C. for 2 hours, the color of the mixture changing from orange to a final deep red. Steam distillation gave a distillate containing recovered 2-chloronitrobenzene, m.p. 32.5° C. Yield, 8%. The remainder of the acid distillate was made alkaline and extracted with ether, the ethereal extract evaporated,

and the residue converted to the acetyl derivative, m.p. 87–88° C. Only a trace of the amine 2-chloroaniline was formed.

The residue in the reaction flask was extracted with acetone, the solvent removed from the extract, and the residue recrystallized from ethanol. Further recrystallizations from aqueous ethanol gave pale yellow needles of 2,2'-dichloroazoxybenzene, m.p. 56–57° C. alone or with an authentic sample. Yield, 43%.

The residue remaining after acetone extraction was dissolved in hot water, the resulting solution cooled and treated with carbon dioxide to yield a red product. This was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. alone or mixed with samples obtained with arsenite. Yield, 1.0%.

Reduction of 2-Chloronitrobenzene with Maltose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 60° C. and a thick paste of maltose (46.1 g., 0.17 mole) in water (50 ml.) was added. The new mixture was refluxed at 89–90° C. for 1½ hours, the color deepening towards the end of the refluxing. It was steam distilled until no more solid material appeared in the distillate. The distillate was filtered, and yielded unreacted 2-chloronitrobenzene, m.p. 33° C. Yield, 11%. The acid filtrate was made alkaline and extracted with ether; removal of the solvent from the extract gave a small residue, which was converted into a small amount of the acetyl derivative of 2-chloroaniline, m.p. 88° C.

The residue in the flask was extracted with acetone, the solvent removed from the extract, and the residue taken up in ethanol. Recrystallization from aqueous ethanol yielded pale yellow needles of 2,2'-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 42%.

Extraction of the residue insoluble in acetone with hot water and treatment of the extract with carbon dioxide gave a red precipitate. Recrystallization from ethanol yielded purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. alone or with samples obtained with arsenite. Yield, 1.2%.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in ethanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer and thermometer. Sodium hydroxide (70 g., 1.75 mole) and water (300 ml.) were added. The reaction mixture was refluxed at 85–86° C. for 3 hours and steam distilled. Unreacted 2-chloronitrobenzene was recovered in 73% yield. No 2-chloroaniline was isolated. Other products were identified as 2,2'-dichloroazoxybenzene (yield, 9%) and chlorotrihydroxydihydrophenazine (yield, 2.3%) by mixed melting point determinations.

An attempt was made to reduce 2-chloronitrobenzene with sodium hydroxide and methanol, the only products isolated being 2-chloroaniline (yield, 0.02%) and unreacted 2-chloronitrobenzene. Yield, 78%.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

2-Chloronitrobenzene (52.5 g., 0.33 mole) was dissolved in ethanol (600 ml.). The mixture was heated to 50° C. and potassium hydroxide (60 g., 1.07 mole) was added slowly. A further portion (60.0 g., 1.07 mole) of potassium hydroxide was added when the temperature had been raised to 60° C. The reaction mixture was refluxed for 3 hours at 87° C. A very vigorous reaction took place.

Steam distillation gave only a trace of recovered 2-chloronitrobenzene; no 2-chloroaniline was precipitated when the steam distillate was made alkaline. The residue in

the reaction flask was extracted with glacial acetic acid. Removal of the solvent from the extract gave a crude red product, which recrystallized from benzene as orange-red needles of 2,2'-dichloroazobenzene, m.p. 138° C. alone or with an authentic sample. Yield, 20%.

The portion of the residue insoluble in glacial acetic acid was treated with ethanol. Removal of the solvent gave crude yellow needles, which were recrystallized from ethanol as pale yellow needles, of 2,2'-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 6%. No phenazine compounds could be detected in the remainder of the residue left after the above extraction.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene (63.4 g., 0.33 mole) was dissolved in hot methanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer, reflux condenser, and thermometer. A freshly prepared solution of sodium arsenite containing arsenic trioxide (56.2 g., 0.28 mole), sodium hydroxide (64.8 g., 1.62 mole), and water (300 ml.) was added. The reaction mixture was refluxed at 81° C. for 2 hours and treated according to the procedure described for 2-chloronitrobenzene, which is summarized in Fig. 1. Unreacted 2,5-dichloronitrobenzene, m.p. 56° C., was recovered in 19% yield, and 2,5-dichloroaniline, m.p. 49° C. alone or with an authentic sample, in 0.6% yield. In the reduction of 2-chloronitrobenzene, residue III was extracted with acetone, but in the reduction of 2,5-dichloronitrobenzene, residue III was extracted with large volumes of hot water, giving a residue, V, and a deep red colored extract, VI, which was treated with carbon dioxide to produce a red precipitate. This material was recrystallized from ethanol to give red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 2.7%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.1%. The residue V was washed with benzene and recrystallized from ethanol to give yellow needles of 2,2',5,5'-tetrachloroazoxybenzene, m.p. 147° C. alone or with an authentic sample, yield, 37%. Treatment of extract XIII with carbon dioxide gave a red precipitate which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 0.5%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.2%. The trichlorotrihydroxydihydrophenazine prepared was very soluble in methanol and glacial acetic acid and insoluble in water. The total yield was 3.2%. The trichlorodihydroxydihydrophenazine had similar solubilities, except that it was only moderately soluble in ethanol. The total yield was 0.3%. As for chlorotrihydroxydihydrophenazine, the two phenazine derivatives obtained here were degraded to phenazine by zinc dust distillation and their structures will be discussed in a forthcoming publication. The analyses are given in Table VI.

Reduction on a large scale.—Several reductions were carried out on a larger scale. The experimental details of a typical example are mentioned in Table I. As indicated, the yield of 2,2',5,5'-tetrachloroazoxybenzene was raised to 78%, but the yields of the phenazines were not greatly changed.

Effect of alcohol.—A series of reductions of 2,5-dichloronitrobenzene (50.0 g., 0.26 mole) was carried out using sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70 g., 1.75 mole) in water (300 ml.), in the presence of various alcohols. The reaction mixtures were refluxed for 2 hours. The results are shown in Table IV.

Reduction of 2,5-Dichloronitrobenzene with Dextrose

A mixture of sodium hydroxide (30.0 g., 0.75 mole), water (270 ml.), and 2,5-dichloro-

nitrobenzene (32.0 g., 0.17 mole) was heated to 60° C. with efficient stirring. A sirup of dextrose (23.0 g., 0.13 mole) in water (15 ml.) was slowly added in small portions. The reaction mixture was heated to 75° C. for 40 minutes and was then steam distilled until the amount of solid coming over in the steam distillate was negligible. The residue was recovered 2,5-dichloronitrobenzene, m.p. 69° C. Yield, 34%. The filtrate was made basic with sodium hydroxide and a light precipitate of 2,5-dichloroaniline was obtained, m.p. 50° C. alone or with an authentic sample. Yield, 1.6%.

The solution remaining in the flask after steam distillation contained brown crystals of 2,2',5,5'-tetrachloroazoxybenzene, which were removed by filtration. The filtrate was discarded. The azoxy compound obtained was treated with large volumes of hot water until all water soluble substances were removed. The crude azoxy compound was recrystallized from ethanol as bright yellow needles, m.p. 147° C. alone or with an authentic sample. Yield, 23%.

The red colored solution containing water soluble materials was cooled and carbon dioxide was bubbled through it for about 10 minutes. A pale brown flocculent precipitate was obtained, which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C. Yield, 1.5%. Calculated for $C_{12}H_7O_3N_2Cl_3$: C, 43.20%; H, 2.12%; N, 8.39%; Cl, 31.89%. Found: C, 43.30%; H, 2.09%; N, 8.33%; Cl, 32.17%.

The alcoholic mother liquor was found to contain another compound, which was purified by fractional crystallization and obtained as bright yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C. Yield, 0.3%. Calculated for $C_{12}H_7O_2N_2Cl_3$: C, 45.38%; H, 2.23%; N, 8.82%; Cl, 33.49%. Found: C, 45.50%; H, 2.25%; N, 9.08%; Cl, 33.65%.

Effect of sodium hydroxide.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (15 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water. The water contents varied from 70 to 400 ml. and the reaction mixtures were refluxed at 80° C. for 40 minutes.

With a 7.5% solution of sodium hydroxide, the yield of the azoxy compound was 78%, that of trichlorotrihydroxydihydrophenazine, 1.6%, and that of trichlorodihydroxydihydrophenazine, 1.3%. With a 10% solution, the yield of the azoxy compound was 77%, that of trichlorotrihydroxydihydrophenazine, 3.4%, and that of trichlorodihydroxydihydrophenazine, 0.6%. Only traces of 2,5-dichloroaniline were isolated in these experiments.

Effect of temperature.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (200 ml.). The reaction mixtures were heated for 40 minutes at varying temperatures (60° to 90° C.). With a temperature of 70° C. the yield of the azoxy compound was 88% and that of trichlorodihydroxydihydrophenazine was raised to 1.9%; 80° C. was the optimum for the best yield of trichlorotrihydroxydihydrophenazine (1.6%).

Effect of Tergitol-08.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (270 ml.). The reaction mixtures were heated to 80° C. for 40 minutes. Tergitol-08 in varying amounts (0.5 to 1.0 ml.) was added. With 0.5 ml. of Tergitol-08, the yield of the azoxy compound was raised by 11%.

Effect of ethanol.—2,5-Dichloronitrobenzene (16.0 g., 0.09 mole) was dissolved in ethanol (40 ml.), and sodium hydroxide (15.0 g., 0.38 mole) and water (100 ml.) were

added. The reaction mixture was heated to 60° C. and a paste of dextrose (11.5 g., 0.06 mole) in water (8 ml.) was added slowly. The mixture was then refluxed at 86–87° C. for 2 hours. Unreacted 2,5-dichloronitrobenzene was recovered in 2.5% yield. Other products isolated were 2,5-dichloroaniline (yield, 6.0%), 2,2',5,5'-tetrachloroazoxybenzene (yield, 60%), and trichlorotrihydroxydihydrophenazine (yield, 2.2%).

Reduction of 2,5-Dichloronitrobenzene with Lactose

2,5-Dichloronitrobenzene was reduced with lactose in alkaline medium and the same procedure as described for the lactose reduction of 2-chloronitrobenzene was employed. The quantities and experimental conditions are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was reduced with maltose using the procedure previously described for 2-chloronitrobenzene. The details of the reduction are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

The procedure followed was the same as the one described for the 2-chloronitrobenzene reduction, except that the refluxing time was 2 hours instead of 3. The alcohols used were methanol and ethanol. The results are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol using the same procedure as described for the corresponding reduction of 2-chloronitrobenzene. The experimental details and yields of products are given in Table V.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—2-Bromonitrobenzene was also reduced with sodium arsenite in alkaline medium. The experimental details are mentioned in Table I. The analysis for the bromotrihydroxydihydrophenazine obtained is given in Table VI.

Reduction with dextrose.—2-Bromonitrobenzene was reduced with dextrose in alkaline medium. The experimental details are given in Table III.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

The details of the reduction of 2,4-dinitrochlorobenzene with sodium arsenite in alkaline medium are shown in Table I. 2,2-Dichloro-5,5'-dinitroazoxybenzene, reddish-yellow colored, crystallizing in needles from ethanol, m.p. 163–164° C., was obtained. Calculated for $C_{12}H_6O_5N_4Cl_2$: C, 40.36%; H, 1.69%; N, 15.69%. Found: C, 40.11%; H, 1.80%; N, 15.40%.

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SOLVOLYSIS IN HYDROGEN AND DEUTERIUM OXIDE

II. STRONGLY SOLVATED SUBSTRATES¹

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ABSTRACT

Rates of solvolysis are presented for a number of polar substrates in light and heavy water from which the rate ratios k_{D_2O}/k_{H_2O} may be obtained. Compounds studied include methyl, *o*-methyl-, *p*-methyl-, *p*-methoxy-, and *p*-fluoro-benzenesulphonate, the α - and β -methylation series of alkyl methanesulphonates, methyl and isopropyl nitrate, methyl phosphate and sulphate, methane- and benzene-sulphonyl chloride, and *t*-butyldimethylsulphonium iodide. The oxyanion esters, despite wide variation in reactivities, show very small variation in the rate ratios which lie near 0.9. The values for the chlorides are 0.63, and for the sulphonium salt, 0.95. The failure of the rate ratios to reflect the mechanistic changes required by variation in the alkyl groups and oxyanions is attributed to the structure of initial state solvation and the easy saturation of *ratio-affecting* structural changes by small charge development in the transition state.

In a recent paper from this laboratory (25) we showed that the rate ratio (k_{D_2O}/k_{H_2O}) for the solvolysis of the esters of strong acids in light and heavy water appears to be characteristic of the anion being produced and varies little, if at all, with changes in the alkyl group. This latter generalization obtains even for differences in those groups which would be expected to result in large changes in the reaction mechanism. The fact that the sulphonic esters tended to give a k_{D_2O}/k_{H_2O} ratio closer to unity than the halides led to the postulate that the classification of esters according to this parameter arose from differences in the initial state solvation. In this paper we extend the investigation to other esters which solvolyze to give oxyanions, and include for comparison several other compounds which also undergo specific solvation in the initial state. These results are interpreted in terms of current hypotheses (13, 14) concerning the nature of aqueous solutions of non-electrolytes and ions.

DISCUSSION

The rather surprising postulate that the k_{D_2O}/k_{H_2O} ratio is more sensitive to solvation differences in the initial state than in the transition state finds further confirmation in the results presented here. Initial state solvation differences arising from the presence of a charge near the seat of reaction are well known to result in large changes in the kinetic parameters characterizing solvolysis (4, 16) but normally such differences are neglected when comparing unchanged esters. As we have noted elsewhere ((33), but see (40)), this omission undoubtedly contributes to the difficulty of setting up satisfactory correlation equations based on relative rates alone.

In the initial state, esters in aqueous solutions may be pictured as surrounded by a flexible solvent envelope, able to accommodate itself to the shape of the substrate but permitting rapid exchange with the bulk solvent. The envelope has frequently been described as an "iceberg", a very graphic term which we shall use but which carries with it the connotation of greater rigidity than obviously exists. In the solution process the most striking evidence for the "iceberg" picture comes from the large positive heat

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capacities which characterize the solution of non-polar molecules in water. This heat capacity is far too large to arise from changes in the degrees of freedom of the substrate and must therefore be attributed to changes in the structure of the solvent. In some cases this change is so large that the partial molal volume of the solute is negative.

The greater order which characterizes the "iceberg" makes possible the absorption of energy by a process roughly analogous to melting. However, in contrast to a true melting process occurring sharply at a single temperature, the existence of a heat capacity of solvation at even relatively high temperatures shows that the "icebergs" are not unique structures as in solid gas hydrates, but are regions of order arising as a consequence of the mere presence of the solute. Lack of any appreciable temperature coefficient in the heat capacity of solution for the non-electrolyte shows that the difference in order between bulk water and water in the "iceberg" changes regularly throughout the liquid range. Similarly, the absence of any definite temperature coefficient for the heat capacity of activation in solvolysis (32, 33) shows that there is again a smooth decrease of the relative order in the transition state solvation shell with increasing temperature.

As reported in Paper I, our limited examination of temperature coefficients gives no indication of a difference in activation energy between the two solvents. However, an increase in ΔH^\ddagger of only 50–70 cal./mole is sufficient to produce a 10% decrease in rate. Even if the decrease in heavy water were due entirely to a $\Delta\Delta H^\ddagger$ of 70 cal./mole, the rate ratio for ΔH^\ddagger of 21 kcal./mole would only change from 0.88 at 5° C. to 0.91 at 100° C. Consequently the use of data at several temperatures, required by widely differing rates and the precision needed, is easily justified. It was surprising to find no difference in ΔH^\ddagger , however, since a small but definite increase in hydrogen-bond energy has been reported for heavy water (12).³ Since $\Delta\Delta H^\ddagger$ and $\Delta\Delta F^\ddagger$ are both small it follows that $\Delta\Delta S^\ddagger$ is likewise small, i.e., that k_{D_2O}/k_{H_2O} is not the resultant of large cancelling ΔH and ΔS terms. However, the lack of a temperature coefficient for the ratio focuses our attention on the structural differences between the two waters from which $\Delta\Delta S^\ddagger$ would arise.

The greater structure of heavy water which can lead to differences in stabilization of both initial and transition states is indicated by many properties (20): e.g. by the larger molal volume of D_2O (at minimum 0.35% greater), by its higher temperature of maximum density (11.2° C.), and by its considerably higher viscosity ($\eta_{D_2O}/\eta_{H_2O} = 1.230$ at 25° C.). Initial state solvation differences are reflected in the lower solubilities in D_2O which may be attributed to the greater difficulty of creating holes in heavy water: nitrobenzene, 90–96% (39); carbon dioxide, 90% (8); iodine, 83% (5); hydroquinone, 83% (21). On the other hand quinone is more soluble in D_2O than in H_2O (21), an indication that substrates that can accept hydrogen bonds can derive enough extra solvation energy in D_2O to offset the larger hole-forming deficit. With such a variety of parameters, any result can be "explained". The rate ratios, however, are too insensitive to structure to permit a choice among the alternatives on their evidence alone. Our interest in them is as an auxiliary requirement to be exacted of mechanisms otherwise derived.

The isotopic solvation effect for the transition states is of course even less simple to predict than for the initial states. Solvation of ions presumably involves strong orientation

³There is a precedent for solvent rearrangement without isotopic heat effect in the absence of such an effect in the heat of dissociation of krypton and xenon hydrates with both waters (15). However, this example involves no polar interaction with the substrate. It would be interesting to see whether the ultraviolet absorption maxima for alkyl nitrates in the two waters are shifted as they are for the nitrate ion (9).

of the appropriate end of the solvent dipole, as in salt hydrates. One might expect anions to be more strongly stabilized by deuterium bonds while for cations the reverse is true because of the lower basicity of D_2O (and hence co-ordinating power, if we neglect steric effects (35)). However, either kind of stronger orientation will disrupt the structure of the next water layer beyond the primary solvation shell (13), breaking up the tetraco-ordination in the region between them. The net effect for anions is that Cl ions are reported to have a slightly smaller heat of solution in heavy water (22) and this trend increases with the size of the anion (23). Relative solubilities for ionic substances are of little help, since most of the examples are for quite soluble materials and specific differences would certainly be obscured in concentrated solutions; however, nearly all salts are less soluble in D_2O (cf. e.g. 6, 11). Conclusions concerning solvation differences of transition states are further complicated by odd-shaped substrates, by varying charge development and separation, by varying degrees of solvent exclusion, and by differing nucleophilic participation during the activation process.

TABLE I
SOLVOLYTIC RATE CONSTANTS FOR ALKYL ESTERS IN HYDROGEN AND DEUTERIUM OXIDE

Ester	Temp.	$k_{H_2O} \times 10^{-3}$, sec. ⁻¹	$k_{D_2O} \times 10^{-3}$, sec. ⁻¹	k_{D_2O}/k_{H_2O}
MeSO ₂ Me ^a	59.996	22.03	20.64	0.937
MeSO ₂ Et	59.993	19.80 ± 0.06	18.33 ± 0.14	0.926
MeSO ₂ i-Pro	29.967	37.10 ± 0.05	34.43 ± 0.12	0.928
MeSO ₂ n-Bu	59.994	14.71 ± 0.04	13.59 ± 0.08	0.924
MeSO ₂ i-Bu	79.994	33.30 ± 0	30.48 ± 0.05	0.922
MeSO ₂ neo-Pen	79.986	16.47 ± 0.06	15.74 ± 0.09	0.956
PhSO ₂ Me ^a	60.622	55.92	50.62	0.905
PhSO ₂ Et ^a	60.627	54.12	49.5	0.915
PhSO ₂ i-Pro ^a	30.103	124.3	114.9	0.924
p-MeC ₆ H ₄ SO ₂ Me ^b	60.000	36.72	32.91	0.896
p-MeC ₆ H ₄ SO ₂ Et	59.995	35.30 ^c	32.98 ± 0.16	0.934
MeNO ₂ ^b	85.103	0.725	0.599	0.83
i-ProNO ₂	79.999	10.24 ± 0.02	9.11 ± 0.02	0.891

^a Paper I.

^b Table II.

^c Calculated from three-constant equation (33).

Despite the range of temperatures dictated by the rates, and the range of alkyl groups, the variation in the ratios for the methanesulphonates (Table I), 0.922 to 0.956, is little more than the probable error of 1–2%. This variation is a substantial fraction of the differences between k_{D_2O} and k_{H_2O} for this series, but it is surprisingly small considering the shifts in mechanism required by the variation in the alkyl groups (24, 31). The absence of any large resultant effect on the ratios therefore indicates that either the changes in solvation as a consequence of changing the alkyl group and presumably the mechanism are small, or we are viewing the resultant of two or more opposing effects. In Paper I we tentatively identified these as ion solvation and "iceberg" disruption effects. To this picture we can now add the observation that the insensitivity of the ratio to differences in the anionoid portion, so long as it is polar, suggests that the structural changes responsible may already be complete at low charge development. This is not to imply that no further structural changes occur with increasing charge development in the transition state, since these are indicated by the differences found in the entropy and heat capacity of activation (33). A more detailed discussion of this series will be given when the ΔC_p^\ddagger s for the hydrolysis in light water are reported (2).

TABLE II

SOLVOLYTIC RATE CONSTANTS AND RATE RATIOS k_{D2O}/k_{H2O} FOR THE HYDROLYSIS OF A SERIES OF METHYL ESTERS (CH_3X) IN HYDROGEN AND DEUTERIUM OXIDE

X	Temp., °C.	$k_{H2O} \times 10^{-5}$, sec. ⁻¹	$k_{D2O} \times 10^{-5}$, sec. ⁻¹	k_{D2O}/k_{H2O}
MeSO ₃ ^a	59.996	22.03	20.64	0.937
Me ₂ PO ₄ ^b	99.993	4.233±0.014	3.964±0.008	0.936
C ₆ H ₅ SO ₃ ^a	60.622	55.92	50.62	0.905
<i>p</i> -MeOC ₆ H ₄ SO ₃	59.950	28.70±0.04	26.29±0.05	0.916
<i>p</i> -MeC ₆ H ₄ SO ₃	60.000	36.72±0.14	32.91±0.13	0.896
<i>p</i> -FC ₆ H ₄ SO ₃	59.982	63.23±0.10	56.72±0.06	0.897
<i>o</i> -MeC ₆ H ₄ SO ₃	59.995	41.80±0.2	38.10±0.05	0.911
MeSO ₄	39.995	93.02±0.12	83.58±0.12	0.899
NO ₃ ^c	85.103	0.725±0.001	0.599	0.83
Cl ^a	89.957	5.64	4.38	0.780
Br ^a	89.947	67.0	54.8	0.816
I ^d	79.986	8.19±0.03	6.68±0.02	0.816

^aData taken from paper I of this series (25).^bPrevious value in H₂O: 3.8×10^{-5} sec.⁻¹ at 100.1° (1).^cPrevious value in H₂O: 0.655×10^{-5} (calc. from equation of Ref. 27).^dData taken from succeeding paper of this series (26).

Anionoid Groups

All of the functional groups in the substrates reported here (Table II) are hydrophilic in varying degrees from the very soluble phosphate to the much less soluble nitrates and sulphonyl chlorides. The nitrate group differs from the sulphonates and the phosphates in being planar and π -bonded to oxygen, while the others are globular and dipolar bonded. The number of charge-bearing ligands (7) is either three or four. However, these details evidently have little effect on the rate ratios, which hardly vary for these esters, neglecting the methyl nitrate, for which our data do not satisfactorily agree with those reported previously (27). Bond energies and ionic solvation as reflected in absolute rates (and in the strengths of corresponding acids) are not the governing features, since the relatively fast-reacting sulphates and sulphonates derived from the strongest acids lie in rate ratio between those of the phosphate and the nitrate esters.

We looked briefly into the question of solvent exclusion by the anionic part, since this was one possible cause for the lower ratio of the benzenesulphonates compared to the methanesulphonates. However, the value for *o*-methylbenzenesulphonate is almost identical with that for benzenesulphonate and slightly higher than that for the *p*-isomer. Also, looking for effects at a distance from the reaction site, we found neither the mildly activating *p*-fluoro nor the deactivating *p*-methoxy substituents to shift the ratio outside the range of the other benzenesulphonate values.

The sulphonyl chlorides are mentioned here because of the initial state interaction with solvent, although the mechanism may be more complicated than simple S_N1 or S_N2. However, neglecting possible pre-equilibria (32), we can attribute the low values for the

TABLE III

SOLVOLYTIC RATE CONSTANTS FOR HIGHLY POLAR COMPOUNDS IN HYDROGEN AND DEUTERIUM OXIDE

Compound	Temp.	$k_{H2O} \times 10^{-5}$, sec. ⁻¹	$k_{D2O} \times 10^{-5}$, sec. ⁻¹	k_{D2O}/k_{H2O}
CH ₃ SO ₂ Cl	20.001	10.90±0.02	6.89±0.03	0.632
PhSO ₂ Cl	10.003	62.84±0.31	39.75±1.0	0.633
<i>t</i> -BuS ⁺ Me ₂	70.019	11.27±0.03	10.70±0.03	0.949
Ph ₂ CHN ⁺ Me ₃	100	<0.01		

ratio ($k_{D_2O}/k_{H_2O} = 0.63$) to the much greater reorientation of solvent involved in the conversion of the sulphonyl group from a negative center to a positive center ($R-SO_2^+$ in Hall's picture (17) of S_N1 here, or $R-SO_2OH_2^+$ for a simple S_N2 mechanism). Diisopropylphosphonyl chloride, however, falls in the ordinary range for the alkyl chlorides ($k_{D_2O}/k_{H_2O} = 0.8$) (10).

Finally, solvolysis of ionic substrates becomes relevant, particularly if charge is dissipated in the transition state. Swain and his co-workers (36) reported provisional data for *t*-butyldimethylsulphonium ion, but they did not decide whether the result lay slightly above or below unity. Somewhat to our surprise we found the ratio to be 0.95. Pritchard and Long, in their paper on the solvolysis of epoxides in both waters (30), attribute the rate reduction in D_2O in their own and Swain's work to increased solvation in the transition state, but do not deal with the sulphonium ion other than to describe the solvation changes as "a slight decrease". The unusually high entropies and energies of activation for solvolysis of the sulphonium ions ((19), p. 242) indicate a more serious reorientation of solvent than this. The change in structure to be expected is a spreading of the ionic solvation shell as the charge disperses. Evidently the effect of the increased number of solvating molecules more than offsets their decreased tightness of binding, an observation which lends support to the previous hypothesis given above of saturation of ratio-affecting structural changes at low charge density. Benzhydryltrimethylammonium ion fails to react appreciably at 100° C. in water. Other ionic materials examined are more appropriate to a future communication on anchimeric substrates.

EXPERIMENTAL

Materials

Methyl and ethyl *p*-toluenesulphonate and methyl *p*-methoxybenzenesulphonate were as reported earlier (31). Methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl methanesulphonate were prepared by the reaction of the corresponding sodium alkoxide (28) on methanesulphonyl chloride, fractionally distilled from the best grade commercial material. Similarly methyl *p*-fluorobenzenesulphonate was prepared from *p*-fluorobenzenesulphonyl chloride. Isobutyl and neopentyl methanesulphonate were made by the Tipson method (37).

Methyl nitrate was prepared by the Organic Syntheses procedure (3) suppressing nitrite formation with sulphamic acid and was purified before use by passage through activated alumina. Isopropyl nitrate was made by a modification of Pattison's method (29), using isopropyl bromide, and benzonitrile instead of acetonitrile to facilitate separation. The slightly yellow product (b.p. 50° C. at 90 mm.) was purified by fractional freezing and passage through alumina.

Methyl sulphate and methanesulphonyl chloride were refractionated from Eastman Kodak White Label material. Benzenesulphonyl chloride of the same grade and source was purified by fractional freezing. A sample of high purity methyl phosphate was kindly supplied by Dr. R. A. B. Bannard, of Defence Research Chemical Laboratories. Tertiary-butyldimethylsulphonium iodide was prepared by the usual method (18) and washed white with ethanol before use. Benzhydryltrimethylammonium bromide was similarly made by reaction of benzhydryl bromide with trimethylamine in nitromethane.

Methyl *o*-methylbenzenesulphonate was prepared by one of us for another purpose (34).

Refractive indexes or melting points are given for these materials in Table IV.

As in the first paper of this series, the linearity of the rate plots serves as an independent criterion for the absence of alternative reactants.

Method

The conductance method of kinetic analysis was described previously (25).

TABLE IV
PHYSICAL CONSTANTS OF ESTERS

n_D^{25}		n_D^{25}	
MeSO ₃ Me	1.4127	Me ₂ SO ₄	1.3873
MeSO ₃ Et	1.4151	Me ₃ PO ₄	1.3939
MeSO ₃ <i>i</i> -Pro	1.4167	MeNO ₃	1.3728
MeSO ₃ <i>n</i> -Bu	1.4255	<i>i</i> -ProNO ₃	1.4132
MeSO ₃ <i>i</i> -Bu	1.4230	MeSO ₂ Cl	1.4500
MeSO ₃ neo-Pen	1.4252	PhSO ₂ Cl	1.5484
<i>p</i> -FC ₆ H ₄ SO ₃ Me	1.4978	<i>t</i> -BuSMe ₂ I	M.p., 175-177 dec.
<i>o</i> -MeC ₆ H ₄ SO ₃ Me	M.p., 28° C.	Ph ₂ CHNMe ₂ Br	M.p., 133.4-135° C.

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DIELECTRIC CONSTANTS OF LIQUID SULPHUR DIOXIDE, ETHYL CHLORIDE, AND ETHYLENE OXIDE¹

J. D. NICKERSON AND R. MCINTOSH

ABSTRACT

Dielectric constants of sulphur dioxide, ethyl chloride, and ethylene oxide have been measured over the frequency range 9 to 92 Mc./second and at temperatures between -35° and $+20^{\circ}$ C. Dipole moments computed from the Debye, Onsager, and Kirkwood equations are reported and compared with the moments which are known from measurements on the gaseous substances.

Measurements of the dielectric constants of the liquid form of low boiling substances such as ethyl chloride, ethylene oxide, or sulphur dioxide have only infrequently been made. Moreover, where measurements have been reported, the values obtained (2, 4, 13) by different investigators do not agree particularly well. The values of the dielectric constants for such substances are useful, among other reasons, for comparison with the values obtained when these materials are employed as the adsorbates on solid surfaces, since the comparison between adsorbed state and bulk liquid is a natural one to make.

In order, therefore, to obtain such data and to gain experience in measuring dielectric constants at frequencies up to 100 Mc./second, ethyl chloride, ethylene oxide, and sulphur dioxide were examined several years ago (9) over a frequency range from about 9 to 92 Mc./second in the temperature range -35° C. to $+20^{\circ}$ C. Since such data do not appear to have been reported since that time and since the values obtained in this investigation are considered correct to about 0.5%, a brief description of the apparatus and procedure, and the values obtained, are given below. Tests of the Debye (3), Onsager (10), and Kirkwood (7) equations are made.

EXPERIMENTAL

A diagram of the cell is given in Fig. 1. F is the ground plate of the test condenser and is moved by the micrometer C. The high potential plate is directly below F and is formed by an evaporated silver film on the glass cell A. Connection is made to the resonance circuit by a contact from the high potential plate into a mercury pool M. B is a double-walled steel tank and N is the thermocouple inlet which also leads to the vacuum system as does O. The glass cell A is sealed at E by means of a gasket. Thus the inside of the cell containing the dielectric can be evacuated separately.

This particular design of cell offered two advantages: (a) no liquid can get behind the plate, which is ungrounded, and introduce errors dependent upon the dielectric constant of the liquid under examination; (b) the movable plate within the liquid permits the circuit to be tuned to resonance so that the general procedure due to Hartshorn and Ward (5) may be employed. In the present arrangement, however, it should be noted that tuning is not performed with an auxiliary air condenser, and thus if the fluid has an appreciable conductance, the necessary condition that capacity may be varied independently of conductance does not exist. For the liquids studied the conductance was sufficiently small that no error resulted.

The advantage of the method invented by Hartshorn and Ward is that an actual measurement of capacity at high frequencies is not required. The assembly is calibrated

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Contribution from the Chemistry Department, University of Toronto, Toronto, Ontario.

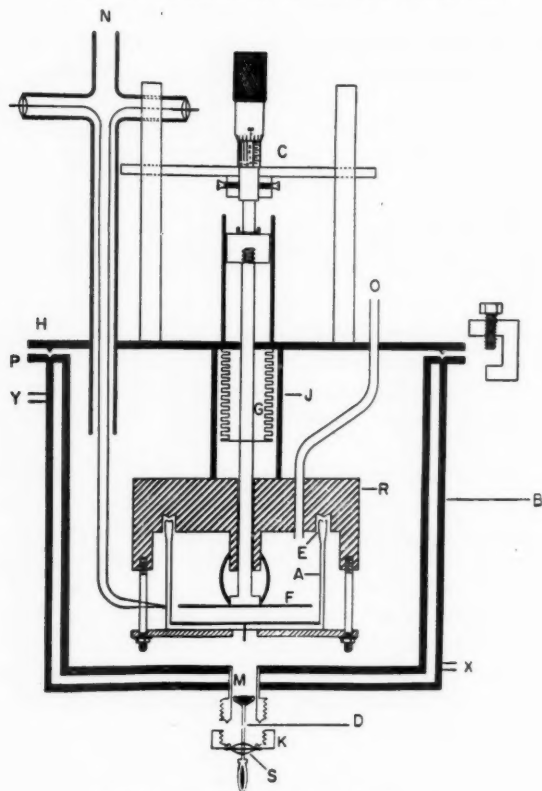


FIG. 1. Diagram of dielectric cell.

at low frequencies and the true values of the capacity are recorded for the positions of the movable plate in terms of the setting of the micrometer. In the present instance the values were obtained by means of a Schering bridge (15) and a General Radio Type 722N Condenser at a frequency of 20 kc./second.

Asymmetry of the resonance peaks using the test cell as tuning condenser was accounted for by a small series inductance term in the measuring condenser, and the position for the resonance condition determined from the corrected (and hence symmetrical) curves. At the highest frequency employed a small fixed condenser of about $10\ \mu\text{f.}$ capacity was inserted in series with the test cell so that the combined capacity would be sufficiently small to permit a condition of resonance. It can readily be shown that for a given frequency this expedient does not affect the validity of the usual procedure of determining the setting of the micrometer at the condition of resonance with a vacuum between the plates and the setting required at the condition of resonance with the unknown liquid between the plates.

Since the capacity between the plates of the condenser, as distinct from the total capacity of the cell, is the number required in obtaining the dielectric constants, the residual capacity was determined as shown in Fig. 2. The value of the total capacity

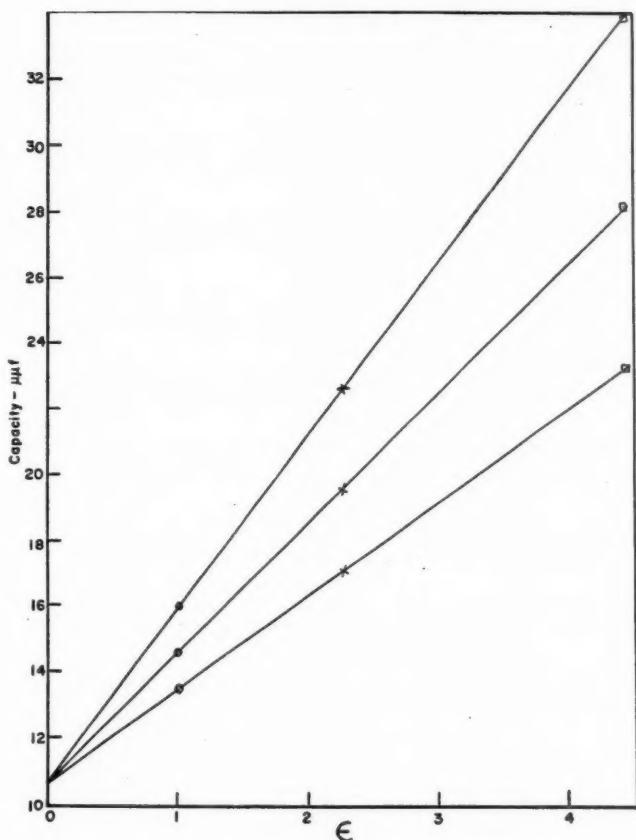


FIG. 2. Illustration of method of obtaining value of capacity between condenser plates.

at various plate settings was determined by using fluids of different and known dielectric constants. The linear plots were then extrapolated back to $\epsilon = 0$, and served to define the residual capacity to $\pm 0.05 \mu\text{f}$.

Since the dimensions of the cell changed with temperature, the capacity of the cell was determined as a function of plate setting over the range of temperature employed.

The gases employed were obtained from the Matheson Chemical Company and were distilled, keeping the middle fraction for use. Their purity was tested by comparing the pressure at several temperatures with vapor pressure data in the published literature (6). No chemical tests of purity were employed.

RESULTS

The results of the measurements of the dielectric constants of three liquids, ethyl chloride, sulphur dioxide, and ethylene oxide, are given in Table I A, B, and C and graphically in Fig. 3. Each has been measured at three frequencies at least between 9 and

TABLE I

Temperature, ° C.	Frequency, Mc./second	Dielectric constant
A. Sulphur dioxide		
6.4	64.0	14.65
-5.5	91.5	15.50
-10.4	48.8	15.90
-18.2	10.3	16.41
-22.0	91.5	16.70
-25.0	64.0	16.95
-30.0	91.5	17.34
-30.0	10.3	17.32
-30.1	48.8	17.35
B. Ethyl chloride		
20.0	41.0	9.45
19.0	90.0	9.52
10.0	90.0	9.92
5.8	9.8	10.14
0.2	41.0	10.41
0.0	90.0	10.43
-4.5	9.8	10.64
-11.0	41.0	11.07
-13.6	9.8	11.26
-19.0	90.0	11.58
-19.8	41.0	11.67
-24.1	9.8	12.04
-35.0	41.0	12.95
-36.0	90.0	13.02
C. Ethylene oxide		
20.0	10.7	12.42
9.7	41.0	13.10
1.1	10.7	13.63
-5.0	92.0	14.10
-10.0	41.0	14.50
-14.8	10.7	14.85
-15.2	92.0	14.88
-20.2	10.7	15.37
-30.0	92.0	16.10
-30.0	41.0	16.11

92 Mc./second, and within the temperature range -35°C. to $+20^{\circ}\text{C.}$ The values are reproducible to ± 0.03 and the temperatures to $\pm 0.06^{\circ}\text{C.}$

In Fig. 3 the data for sulphur dioxide form a straight line while the ethyl chloride plot is slightly curved. For ethylene oxide the representation appears slightly curved down to 0°C. but below this temperature it is linear.

For ethyl chloride the empirical equation

$$10.43 - 0.056t + 0.000418t^2 = \epsilon,$$

where t is in $^{\circ}\text{C.}$, serves to represent the results within ± 0.03 for the value of ϵ .

In the case of sulphur dioxide the curve may be represented by the equation

$$15.12 - 0.072t = \epsilon.$$

Below 0°C. the data for ethylene oxide are satisfactorily represented by the equation

$$13.71 - 0.075t = \epsilon.$$

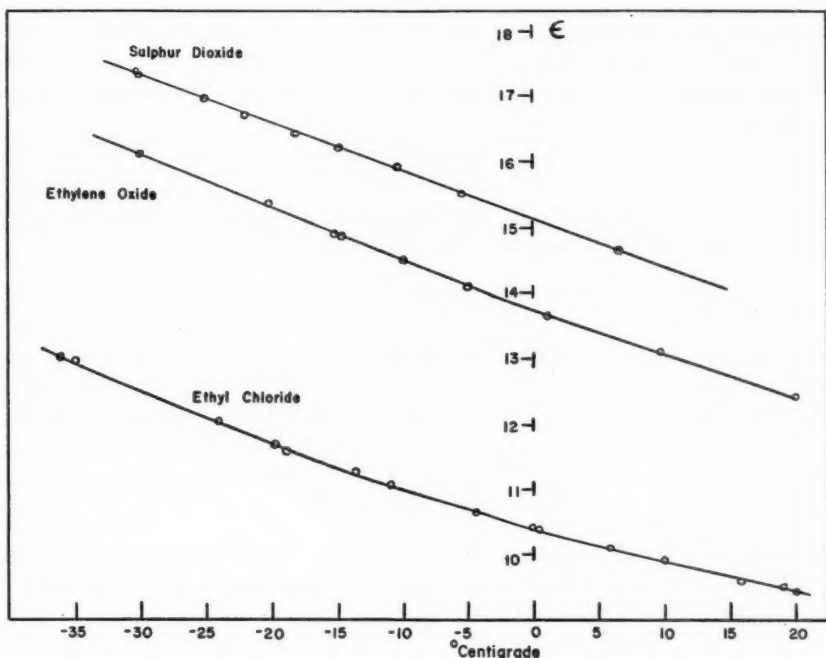


FIG. 3. Values of dielectric constants as a function of temperature.

DIPOLE MOMENTS

The value of the orientational polarization for the liquid state was calculated using the Debye equation (3)

$$P_0 = \frac{M}{\rho} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right).$$

From this result the dipole moment was calculated. The refractive indices used were those recorded for the sodium D-line. The error incurred in the use of these indices rather than that at infinite wave length is small. The temperature values and the dielectric constants were taken from the dielectric constant vs. temperature curves as previously given.

The results show that the calculated moments in all three cases vary with temperature and do not agree with recorded values of the moments for the gases.

Using the following arrangement of the Onsager (10) equation, the orientational molar polarization P_0 was again computed and subsequently the gaseous dipole moment μ_0 from the second of the following equations:

$$P_0 = \frac{M}{\rho} \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}$$

and

$$\mu_0 = \sqrt{\frac{9kT}{4\pi N}} P_0$$

where N = Avogadro's number,
 k = Boltzmann's constant,
 and T = absolute temperature.

The liquid dipole moment μ was computed from the Onsager expression relating μ and μ_0 , that is,

$$\mu = \frac{(n^2+2)(2\epsilon+1)}{3(2\epsilon+n^2)} \mu_0.$$

Similar calculations were also made assuming the following arrangement of the Kirkwood equation which has been applied to polar liquids (11, 12):

$$P_0 = \frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon} \frac{M}{\rho} = \frac{4\pi N}{3} \left(\alpha + \frac{g\mu^2}{3kT} \right).$$

Here g is a parameter, the difference of which from unity is the measure of the influence of a molecule upon its neighbors.

$g^{\frac{1}{2}}\mu$ may be obtained from a P_0 vs. $1/T$ plot and the value of $g^{\frac{1}{2}}\mu_0$ or gaseous dipole moment can then be calculated from the Onsager equation,

$$g^{\frac{1}{2}}\mu_0 = \frac{3(2\epsilon+n^2)}{(n^2+2)(2\epsilon+1)} g^{\frac{1}{2}}\mu,$$

owing to similarity of the models.

Table II gives the results of the calculated average moment for the Onsager and Kirkwood equations from -35°C. to $+20^\circ\text{C.}$

TABLE II
DIPOLE MOMENT CALCULATIONS

	Onsager μ_0	Kirkwood $g^{\frac{1}{2}}\mu_0$	Observed μ_0
Ethyl chloride	1.96 D.	2.17 D.	2.03 D. (Ref. 14)
Ethylene oxide	1.92 D.	—	1.89 D. (Ref. 1)
Sulphur dioxide	1.93 D.	1.69 D.	1.62 D. (Refs. 8, 16)

The Onsager result for sulphur dioxide does not agree with the observed value and shows a definite temperature dependence. Here the Kirkwood result is definitely in better agreement with the observed moment than that calculated by the Onsager expression.

The moments for ethyl chloride and ethylene oxide do appear, on the other hand, to be satisfactorily expressed by the Onsager equations. The Kirkwood result for ethyl chloride is somewhat high but if the use of n^2 for ϵ_∞ is a source of error, then by estimating this error, a value for $g^{\frac{1}{2}}\mu_0$ of 2.08 D. can be obtained.

SUMMARY

The values of the dielectric constants of ethyl chloride, sulphur dioxide, and ethylene oxide have been determined in the temperature range of -35°C. to $+20^\circ\text{C.}$ and a frequency range of 9 to 92 Mc./second using a resonance method.

Calculations of dipole moments have indicated that the Debye expression does not give satisfactory results. The equations suggested by Onsager give reasonable agreement

between calculated and observed gaseous dipole moments for ethyl chloride and ethylene oxide. The results for sulphur dioxide have been found to be best represented by the equations given by Kirkwood.

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THE SOLUBILITY OF MALACHITE¹

J. F. SCAIFE²

ABSTRACT

The solubility at 25° C. of the sparingly soluble basic copper carbonate malachite has been determined by two methods. The constancy of the calculated value of the solubility product in solutions of varying ionic strength has shown it to be a comparatively well-defined material suitable for the study of the complexing ability of various organic chelating compounds. Evidence is presented for the existence of a cupric ion-carbonate ion complex under appropriate pH conditions.

INTRODUCTION

A method for the determination of the dissociation constant of metal chelates is that of equilibration with a sparingly soluble salt of the metal. In this manner the concentration of the metal ion in question is always known under the conditions defined by the experiment. Malachite has been examined with this object in mind. Copper carbonate, CuCO_3 , apparently does not exist naturally, nor does it seem to have been isolated. Two basic carbonates exist as minerals: malachite, $\text{CuCO}_3\text{Cu}(\text{OH})_2$, and azurite, $2\text{CuCO}_3\text{Cu}(\text{OH})_2$. The composition of the precipitates formed when a solution of a copper salt is added to a solution of sodium carbonate or sodium bicarbonate has been studied by several workers, and the existence of a whole range of basic carbonates has been reported. If these precipitates are, in fact, definite compounds, they do not seem to be stable but seem to change more or less slowly into malachite when kept in contact with the mother liquor (10, 11). A similar observation was made by Free (5); the precipitates formed initially in the presence of carbon dioxide were also found to be $1\frac{1}{2}$ to 3 times as soluble as the malachite finally formed after 4-5 days standing.

The only data in the literature on the solubility of malachite in water or salt solutions were published by Free (5). He determined the amount of copper and total carbon dioxide after equilibrating malachite with various solutions in the presence of various amounts of dissolved CO_2 at 30° C. When suitable corrections are made, it is possible to calculate the solubility product of malachite from Free's data (Table I).

MATERIALS AND METHODS

All reagents were of Analar grade and were tested for the presence of copper before use.

Trace quantities of copper were estimated by a slight modification of the method of Eden and Green (4).

Solutions of sodium bicarbonate were prepared from carefully dried, recrystallized sodium carbonate by dissolving it in a small amount of water and saturating the solution with pure carbon dioxide.

Carbon dioxide when used alone was obtained from "Sparklet" cylinders, and was found never to contain less than 99.9% of CO_2 . The various gas mixtures used in the course of the work were either purchased specially or prepared in gas cylinders in the laboratory. In both cases, the composition of the mixtures was determined before use by means of the Haldane apparatus; the analyses are believed to be accurate to within 0.1% by volume.

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The Preparation of Malachite

The method of preparing malachite was similar to the one used by Free (5). To a solution of 50.4 g. NaHCO_3 in 1600 ml. of water, previously saturated with pure CO_2 , was added slowly and with stirring a solution of 50 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 400 ml. of water. The mother liquor consequently contained NaHCO_3 at a concentration of 0.1 *M*, and its pH was approximately 6.7. The mixture was kept saturated with CO_2 and allowed to stand for at least a week at 25° C. During this time the original bulky precipitate changed to a fine, dense, dark-green powder. The material was washed by decantation to free it, as far as possible, from the smaller particles it contained, and washing was continued until it was free from sulphate and sodium ions. The washing water was saturated with CO_2 before use. The powder was air-dried and usually contained an amount of water corresponding approximately to 1.5 molecules per molecule of malachite. Analyses by the usual methods showed it to contain copper and carbon dioxide in the ratio of 2.000:1.020; a similar excess of CO_2 was reported by Free (5). This excess appeared to be associated with the water contained in the material, for if the solid was dried at 80° C. for 12 hours the exact 2:1 ratio was obtained. Microscopically, the powder consisted of regular spherulites showing double refraction.

The Experimental Determination of Solubility

The solubility of malachite was determined by two different methods: firstly, by estimating the concentration of dissolved copper after equilibrating the solid with water or solutions of sodium chloride in the presence of different partial pressures of CO_2 ; and secondly, by utilizing the manometric technique of Warburg (19) and calculating the amount of dissolved copper from the change in CO_2 pressure when solid malachite was added to water or salt solutions in the presence of different partial pressures of CO_2 .

(1) *Chemical determination of solubility.*—The reaction vessel used for equilibrating solid and liquid (50 ml.) is shown in Fig. 1. Shaking and passage of gas was continued slowly for 8–12 hours, when equilibration had been obtained. A portion of the solution

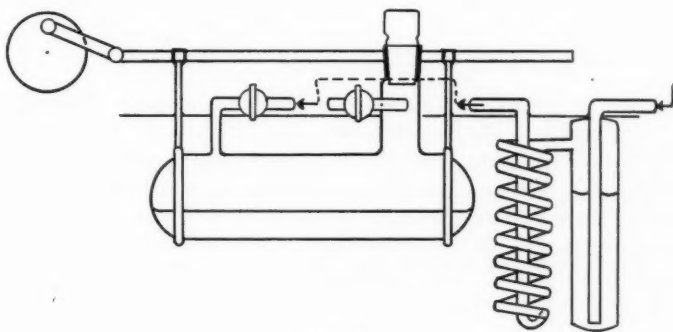


FIG. 1

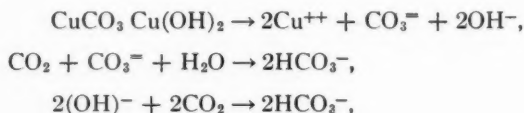
was removed directly from the vessel by means of a fine sintered-glass filtering stick. The analyses for copper on these solutions are believed to be accurate to within 0.05 μg . Cu per ml. The results obtained were independent of the relative amounts of malachite and solution equilibrated together over a wide range but it was desirable to use more than 50 mg. of solid per 50 ml. of solution. If less malachite was present, the time required for equilibration was inconveniently long and—a more serious defect—the smaller

particles of the powder were eroded to such an extent that they tended to become colloiddally suspended in the solution.

(2) *Manometric determination of solubility.*—The precautions to be taken when using the manometric technique of Warburg have been described (3, 18). The Warburg vessels were calibrated (a) by filling with mercury in the usual manner, and (b) by measuring the pressure changes caused by the addition of excess acid to a solution containing a known amount of NaHCO_3 in the presence of CO_2 , or (c) by the addition of an excess of amidosulphonic acid to a solution of NaNO_2 (1). All three methods gave results that agreed to within 1%, but the agreement between the results of the two gasometric methods was still closer (within 0.5%). The volume changes calculated from the difference between the steady pressures observed before and after mixing agreed in duplicate experiments to within 0.5 $\mu\text{l.}$ of CO_2 .

Calculation of the Solubility Product

In the above methods, (1) and (2), the amount of dissolved copper will not correspond exactly to the change in the concentration of bicarbonate ions or, in (2), to the change of CO_2 pressure, and a small correction must be applied. The reason for this correction is that the solution of malachite disturbs the equilibrium between the concentrations of dissolved CO_2 , hydrogen ions, and bicarbonate ions. This unbalance is redressed by the reverse reaction, $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$, proceeding to a small extent. The net effect is that the increase in bicarbonate concentration, or in (2) the decrease in CO_2 pressure, is slightly less than equivalent to the amount of copper dissolving according to the equations given below. This effect is corrected for by a series of successive approximations. At the pH of the solutions here employed the following reactions are assumed to take place:



or collectively:



The agreement between the results of the chemical and manometric estimations indicates that these reactions are the chief ones to occur.

The stoichiometric solubility product, S , of malachite is given by equation [1]; the value of S for any salt varies with the ionic strength of the solution.

In this equation, and succeeding ones, square brackets are used to denote concentrations (moles per liter) and parentheses to denote thermodynamic activities. m^\pm is the mean molarity; the present measurements are not sufficiently accurate to warrant expressing the results as moles per 1000 g. of water.

$$S = [\text{Cu}^{++}]^2[\text{CO}_3^{--}][\text{OH}^-]^2 = (m^\pm)^5. \quad [1]$$

The thermodynamic solubility product, S_o , is given by the equation

$$S_o = (\text{Cu}^{++})^2(\text{CO}_3^{--})(\text{OH}^-)^2 = (f^\pm)^5(m^\pm)^5, \quad [2]$$

where f^\pm is the mean ion activity coefficient. By means of equations [3], [4], and [5], which give the first and second thermodynamic constants of carbonic acid and the

dissociation constant, K_w , of water, equation [1] is expressed in the form of equations [6] and [7]:

$$K_1 = (H^+)(HCO_3^-)/CP, \quad [3]$$

where C = the Henry's law constant for CO_2 and pure water,

P = pressure of CO_2 in atmospheres;

$$K_2 = (H^+)(CO_3^{2-})/(HCO_3^-), \quad [4]$$

$$K_w = (H^+)(OH^-), \quad [5]$$

$$So = K_1 K_2 K_w^2 C (Cu^{++})^2 P / (H^+)^4, \quad [6]$$

$$pSo = pK_1 + pK_2 + 2pK_w - 2 \log(Cu^{++}) - \log CP - 4pH. \quad [7]$$

At 25° C. pK_1 was taken as 6.37 (17) and C , the Henry's law constant, as 0.03395 moles per liter per atmosphere (14); pK_w was taken as 13.72 and pK_2 as 10.25 (13). Equation [7] then reduces to the equation

$$pSo = 44.06 - 2 \log(Cu^{++}) - \log CP - 4pH. \quad [8]$$

Since the concentration of HCO_3^- in the solutions could be calculated from the experimental results, the pH of the solutions was obtained from equation [9], where $fHCO_3^-$ is the individual ion activity coefficient of the bicarbonate ion and

$$\begin{aligned} (HCO_3^-) &= [HCO_3^-] \cdot fHCO_3^-, \\ pH &= pK_1 + \log([HCO_3^-]/CP) + \log fHCO_3^-. \end{aligned} \quad [9]$$

The value of $fHCO_3^-$ was obtained from the Debye-Hückel equation [10], where μ is the ionic strength of the solution and the value of a for the bicarbonate ion is taken as 4.3×10^{-8} , as suggested by Kieland (12):

$$-\log fHCO_3^- = 0.504\sqrt{\mu}/(1 + 3.28 \times 10^7 a \sqrt{\mu}). \quad [10]$$

If the individual activity coefficient of the cupric ion is obtained in a similar way from the equation

$$-\log fCu^{++} = 2.02\sqrt{\mu}/(1 + 3.28 \times 10^7 a \sqrt{\mu}), \quad [11]$$

pSo can be calculated since the concentration of Cu^{++} is known from the experimental results, and $(Cu^{++}) = fCu^{++}[Cu^{++}]$. This procedure has been followed using the value of $a(6 \times 10^{-8})$ suggested by Kieland (12) for the cupric ion.

An alternative method for the calculation of pSo has been attempted which is not so dependent on the use of individual ion activity coefficients. Davies (2) has proposed, following Guggenheim (6, 7), an extension of the Debye-Hückel equation that represents the mean ionic activity coefficients of an electrolyte at 25° C. by the equation

$$-\log f^\pm = 0.5Z_1 \cdot Z_2 \{ [\sqrt{\mu}/(1 + \sqrt{\mu})] - 0.2\mu \}, \quad [12]$$

where Z_1 and Z_2 are the valences of the constituent ions. As malachite provides three ionic species, it is necessary to modify this equation; f^\pm is then given by the equation

$$-5 \log f^\pm = 7 \{ [\sqrt{\mu}/(1 + \sqrt{\mu})] - 0.2\mu \}. \quad [13]$$

The thermodynamic solubility product, So , could then be obtained from equation [2]. Unfortunately the experimental results do not give the concentration of carbonate and hydroxyl ions existing in the solutions, and to calculate them from the bicarbonate

concentration and the pressure of CO_2 it is necessary to make use of equation [14] in which dashes are used to indicate the apparent dissociation constants for the particular solutions employed:

$$So = (f^{\pm})^5 (m^{\pm})^5 K_2' (K_w')^2 / (K_1')^3 \cdot [\text{Cu}^{++}]^2 [\text{HCO}_3^-]^4 / (C')^3 P^3. \quad [14]$$

The values of K_1' in solutions of NaCl up to an ionic strength of unity have been determined (8, 9), but the variation of the other apparent dissociation constants with ionic strength does not seem to be known with equal precision. If, as an approximation, the thermodynamic dissociation constants are used in their place in equation [14], the values of So calculated by both methods are in good agreement at the lower ionic strengths employed, as would indeed be expected.

RESULTS

Table I gives the values of the solubility product of malachite calculated from the data of Free (5). He calculated the free CO_2 by subtracting from the total an amount corresponding to a ratio of dissolved copper to combined CO_2 of 2:1. This assumption

TABLE I
THE SOLUBILITY PRODUCT AT 30° C. CALCULATED FROM THE DATA OF FREE (1908)

Concentration of NaCl (M)	$[\text{Cu}^{++}]$ ($M \times 10^{-4}$)	$[\text{HCO}_3^-]$ ($M \times 10^{-3}$)	CP ($M \times 10^{-2}$)	pH	μ	pSo
0	4.405	0.891	1.886	5.027	0.0013	32.522
0	4.876	0.985	2.110	5.021	0.0014	32.415
0	5.300	1.071	2.553	4.974	0.0015	32.450
0	5.474	1.111	2.699	4.965	0.0016	32.440
0	5.555	1.121	2.798	4.953	0.0017	32.462
0	6.245	1.262	3.427	4.915	0.0019	32.432
1.71×10^{-4}	5.98	1.208	3.097	4.940	0.00197	32.419
8.55×10^{-4}	5.51	1.112	2.547	4.987	0.00251	32.406
1.71×10^{-3}	5.66	1.144	2.924	4.935	0.00341	32.558
8.55×10^{-3}	6.13	1.237	2.760	4.976	0.0104	32.479
0.171	9.12	1.833	2.857	5.046	0.174	32.414

is incorrect; the correct ratio would be practically 1:1 under the conditions of his experiments, the copper in solution existing almost entirely in the form of dissociated copper bicarbonate.

The values of pSo calculated by the first method above from measurements on one sample of malachite are set out in Tables II and III.

TABLE II
THE CHEMICAL DETERMINATION OF THE SOLUBILITY OF MALACHITE AT 25° C.

P (atm.)	Concentration of NaCl (M)	Dissolved copper ($\mu\text{g. per ml.}$)	$[\text{Cu}^{++}]$ ($M \times 10^{-4}$)	$[\text{HCO}_3^-]$ ($M \times 10^{-3}$)	pH	μ	pSo
0.9688	0	47.2	7.425	1.495	5.005	0.0022	31.956
0.3875	0	28.8	4.530	0.912	5.193	0.00139	31.997
0.1938	0	20.2	3.178	0.640	5.343	0.00098	31.985
0.0484	0	10.0	1.574	0.339	5.674	0.00049	31.840
0.9688	0.05	61.7	9.71	1.952	5.056	0.0527	31.982
0.9688	0.10	71.0	11.17	2.244	5.092	0.1033	31.878
0.9688	0.20	77.9	12.26	2.462	5.105	0.2031	31.907

TABLE III
 THE MANOMETRIC DETERMINATION OF THE SOLUBILITY OF MALACHITE AT 25° C.

<i>P</i> (atm.)	Concentration of NaCl (<i>M</i>)	Volume of CO ₂ absorbed (μl. per ml. of solution)	[Cu ⁺⁺] (<i>M</i> × 10 ⁻⁴)	[HCO ₃ ⁻] (<i>M</i> × 10 ⁻³)	pH	<i>μ</i>	p <i>S</i> _o
0.9688	0.05	31.2	10.22	2.054	5.078	0.0527	31.849
0.9688	0.10	34.8	11.33	2.276	5.099	0.1033	31.839
0.9688	0.20	41.4	12.91	2.592	5.128	0.2031	31.771

The Solubility of Malachite in Solutions of Sodium Bicarbonate

The solubility of malachite in solutions of 0.01 to 0.18 *M* sodium bicarbonate is far too small to be measured manometrically with any accuracy even in the presence of approximately one atmosphere of carbon dioxide but it can still be measured chemically using the trace element technique. When this was done, it was found that the amount of copper in solution was much greater than the amount of cupric ion calculated by means of equation [7]. In some cases, depending on the bicarbonate concentration and the pressure of carbon dioxide, the observed value was several thousand times greater than the expected value. There seemed little doubt that ionic association (or complex formation) was occurring between cupric and bicarbonate ions.

By analogy with the complexes of cupric ion and acetate ion that are known to exist in solution (16), the possible modes of combination of cupric and bicarbonate ions and their respective equilibria would seem to be represented by equations [15] to [18]. These equations are expressed in terms of concentrations.



and



$$K_3' = [\text{Cu}^{++}] [\text{HCO}_3^-] / [\text{CuHCO}_3^+] \quad [17]$$

$$K_4' = [\text{CuHCO}_3^+] / [\text{CuCO}_3] [\text{H}^+]. \quad [18]$$

From these equations it follows that

$$[\text{CuCO}_3] = 1/[\text{H}^+] K_4' \cdot [\text{Cu}^{++}] [\text{HCO}_3^-] / K_3' \quad [19]$$

and since

$$[\text{Cu}_T] = [\text{CuCO}_3] + [\text{CuHCO}_3^+] + [\text{Cu}^{++}] \quad [20]$$

$$\text{let } y = ([\text{Cu}_T] - [\text{Cu}^{++}]) / [\text{Cu}^{++}] [\text{HCO}_3^-] = 1/K_3' + 1/[\text{H}^+] K_4' K_3' \quad [21]$$

where $[\text{Cu}_T]$ is the concentration of total copper in solution and $[\text{Cu}^{++}]$ is the concentration of cupric ions calculated from equation [7].

If the experimental results can be represented in terms of these equations, it follows that a straight line should be obtained when *y* is plotted against the reciprocal of the hydrogen ion activity (as given by $\log(\text{H}^+) = -\text{pH}$) as long as the ionic strength is not too high. Moreover, $1/K_3'$ should be given by the intercept of the line on the *y* axis, and $1/K_3' K_4'$ by the slope of the line. The results of the experiments are set out in Table IV, and the plot of *y* against $1/(\text{H}^+)$ is shown in Fig. 2.

It will be seen that the points lie nearly on a straight line, especially in the case of the solutions of low ionic strength. Since the intercept of the line on the *y* axis is almost zero, and such that K_3' is almost certainly greater than 2.5×10^3 , it is concluded that

TABLE IV
SOLUBILITY OF MALACHITE IN SOLUTIONS OF $\text{NaHCO}_3 + \text{CO}_2$

P (atm.)	HCO_3^- (M)	Total Cu ($M \times 10^{-4}$)	Calculated [Cu^{++}] (M)	$1/(\text{H}^+) \times 10^7$
0.3875	0.01	1.07	5.37×10^{-6}	0.173
0.0484	0.01	0.49	2.64×10^{-7}	1.29
0.9688	0.02	2.98	7.16×10^{-6}	0.124
0.3875	0.02	1.21	1.81×10^{-6}	0.311
0.0484	0.02	0.50	8.04×10^{-8}	2.48
0.3875	0.04	1.32	5.75×10^{-7}	0.596
0.0484	0.04	0.59	2.52×10^{-8}	4.75
0.3875	0.08	1.45	1.92×10^{-7}	1.13
0.0484	0.08	0.88	8.47×10^{-9}	9.02
0.0484	0.18	2.63	2.48×10^{-9}	18.7
0.3875	0.04 0.20 NaCl	1.80	1.29×10^{-6}	0.51

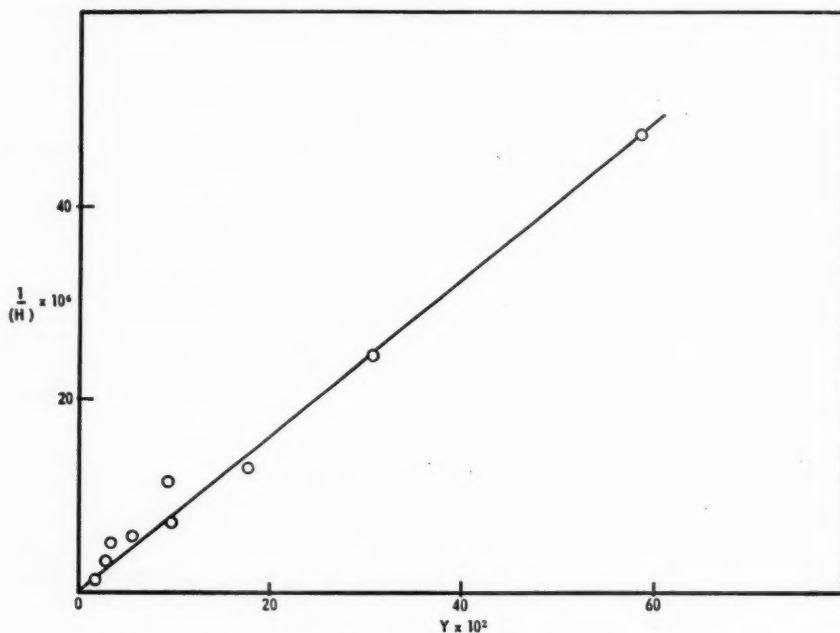


FIG. 2

CuHCO_3^+ is practically completely dissociated and that the excess copper in solution is in the form of the comparatively stable ion pair, $\text{Cu}^{++}\text{CO}_3^-$, to an overwhelming extent. From the slope of the curve,

$$1/K_3' K_4' = 1.24 \times 10^{-4} = K_5' = [\text{CuCO}_3][\text{H}^+]/[\text{Cu}^{++}][\text{HCO}_3^-] \quad [22]$$

and $\text{p}K_5' = 3.91$.

The very small amounts of dissolved copper in solutions containing sodium bicarbonate make it difficult to determine them experimentally. The agreement shown in Table V

between the observed values of total copper and those calculated from equation [22] taking pK_s' as 3.91 is probably, therefore, as close as could be expected.

TABLE V
OBSERVED AND CALCULATED COPPER CONCENTRATIONS IN
 $\text{NaHCO}_3 + \text{CO}_2$ SOLUTIONS

P (atm.)	$[\text{HCO}_3^-]$ (M)	pH	Concentration of total copper ($M \times 10^{-4}$)	
			Observed	Calculated
0.9688	0.02	6.095	2.98	3.01
0.3875	0.08	7.052	1.45	2.25
0.3875	0.04	6.775	1.32	1.82
0.3875	0.01	6.237	1.07	1.73
0.3875	0.02	6.493	1.21	1.63
0.0484	0.18	8.272	2.63	1.07
0.0484	0.08	7.955	0.88	0.79
0.0484	0.04	7.677	0.60	0.62
0.0484	0.02	7.395	0.50	0.52
0.0484	0.01	7.110	0.49	0.46

DISCUSSION

When the difficulties attending the estimation of the solubility product of sparingly-soluble salts containing multivalent ions are considered, it is concluded from the agreement between the values of pSo determined at different ionic strengths (and pressures of carbon dioxide) that the results are as close as could be expected, and that malachite is a comparatively well-defined material.

The slightly lower values of pSo obtained in this work, as compared to those calculated from the data of Free (5), may be a reflection of the different temperature employed, negative solubility coefficient, or the fact that the dissociation constants holding at 25° C. were used in the calculations.

The results also indicate that association in these solutions between cupric and chloride ions to give CuCl_2 or CuCl^+ is slight enough to be neglected up to a concentration of 0.2 N NaCl . Davies (2) has considered that the assumption of complete dissociation of CuCl_2 up to a concentration of 0.005 N CuCl_2 was unlikely to cause very serious errors. Monk (15) calculated the average dissociation constant of CuCl^+ as 0.4 at 25° C. from measurements on the solubility of copper iodate. The present results suggest that the value of the dissociation constant might be even higher.

Eleven different samples of malachite were prepared and the solubility of each sample was determined in at least one of the solutions described in Table II. In general, there was very good agreement between the behavior of the different samples but one of them was found to have a higher solubility than could be explained by experimental errors. A small variation in the solubility of different samples of cupric iodate has been observed (15), and was attributed to variations in particle size.

The failure of equation [7] to predict the amount of soluble copper in solutions containing carbonate can not be attributed to an error in the value of pSo . Uncertainties in pSo arising from the particular values of the constants, K_1 , K_2 , etc., employed in its calculation would only affect the absolute value of pSo ; they would have no effect on the calculated concentration of cupric ions since these constants disappear during the latter calculation. The effect of the main cause of uncertainty in pSo —the values of the individual activity coefficients of cupric ion—was eliminated to some extent when

solutions of sodium chloride alone were compared with solutions of NaHCO_3 of the same ionic strength; the amount of copper in the solutions of bicarbonate was still far greater than the calculated value for cupric ion.

It is evident that the results of Tables IV and V make it imperative to consider what proportion of the measured copper existed in the form of a complex in the solutions of water or NaCl employed in the original solubility determinations. In the calculation of pS_o it was assumed that all the copper found was present as Cu^{++} ; the calculation would be invalidated if a significant degree of association existed. However, the use of equation [22] shows that in these solutions (in which the concentration of bicarbonate ions was very low) the proportion of copper in the form of the complex is small. For example in water saturated with approximately 1/20 atm. of CO_2 the relative concentration of Cu^{++} and CuCO_3 is almost 50 to 1, and the disproportion is even greater in the other solutions. It would be possible to recalculate pS_o on this basis, and in turn to recalculate pK_s' , but it is believed that the experimental accuracy of the methods used hardly warrants these small corrections.

SUMMARY

The solubility of malachite at 25° C. in solutions of varying ionic strength, and under varying partial pressures of carbon dioxide, has been determined by two methods. The most probable value of the thermodynamic solubility product expressed as pS_o is 31.900.

In the presence of carbonate ions, cupric ions tend to form a stable association complex.

ACKNOWLEDGMENT

I wish to record my appreciation for the encouragement and guidance of Dr. J. Brooks during the course of this work.

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KINETICS OF THE PHOTOCHLORINATION OF MONOCHLOROMETHYL CHLOROFORMATE IN THE GAS PHASE¹

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ABSTRACT

The general features of the mechanism of the over-all process $\text{CH}_2\text{Cl}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{Cl}_2 + h\nu$
 $= \text{CHCl}_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{HCl}$ are similar to those for the over-all process $\text{CH}_3-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$
 $+ \text{Cl}_2 + h\nu = \text{CH}_2\text{Cl}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{HCl}$ studied previously. The reaction is inhibited by HCl. Chains are terminated by two processes, one of which is first order, the other second order in atomic chlorine. The first order process is not entirely diffusion controlled and a theory is advanced to account for its nature; the homogeneous combination of chlorine atoms requires a third body, mono- and di-chloromethyl chloroformate being particularly effective. The activation energy for hydrogen abstraction from monochloromethyl chloroformate by atomic chlorine is 5.2 kcal. per mole. The C—H bond dissociation energy in monochloromethyl chloroformate is estimated to be 99.8 ± 4.5 kcal. per mole.

INTRODUCTION

Previous communications from this laboratory (2, 1) have dealt with the photochlorination of methyl chloroformate (RH_3) in the gas phase and in carbon tetrachloride solution. In the present investigation we have studied the kinetics of the formation of dichloromethyl chloroformate (RHCl_2) from monochloromethyl chloroformate (RH_2Cl).

As in the earlier studies, it was found that both first and second order chain termination take place. To establish the nature of these reactions with certainty it was necessary to measure changes in chlorine concentration with great precision, particularly when the chlorine concentration was much greater than that of RH_2Cl . These changes were measured photometrically using the photolysis beam and a specially constructed photometer sensitive to approximately 0.01%.

From observed temperature coefficients it was possible to calculate the activation energy for hydrogen abstraction from RH_2Cl by chlorine atoms and to estimate the C—H bond dissociation energy in the same compound.

EXPERIMENTAL

Reagents

Commercial tank chlorine was dried with phosphorus pentoxide and subjected to 10 trap-to-trap distillations in which only the intermediate portions were retained. Twenty additional distillations were made to remove traces of oxygen before storing the gas over liquid air. Commercial hydrogen chloride was treated in the same way. The RH_2Cl was prepared as described previously (2), degassed as described above, and stored over liquid air.

The Reaction System

The reaction took place in a cylindrical pyrex vessel 25.8 cm. long and 4.08 cm. in diameter (both dimensions internal), with plane pyrex windows. A short length of 2 cm. diameter pyrex tubing was ground to fit the outside contour of the cell and joined to it with Aeraldite cement. By placing liquid air in this tube the cell contents could be

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frozen out. Two metal valves (Hoke No. 411) were connected to the cell through Kovar seals. One of these was connected to a small pyrex finger into which the chlorine could be frozen temporarily after its transmission had been measured and before the addition of the RH_2Cl . The other valve was connected to the high vacuum system. With both valves closed the volume of the cell was $340 \pm 0.25\%$ cm^3 , of which 337 cm^3 could be illuminated by the parallel beam.

The pressure of RH_2Cl in the cell was measured with a spoon gauge and optical lever with an accuracy of $\pm 0.04 \text{ mm}$. Precautions were taken to prevent mercury vapor from coming in contact with the cell and the reagents. The cell was surrounded by a close-fitting double-walled copper jacket made in two halves. It extended 6 cm. beyond each end of the cell and was fitted with pyrex windows. The jacket was well insulated and its temperature was controlled by circulating water through it from a thermostat.

The Optical System

A diagram of the optical system with the reaction cell (RC) and jacket (J_2) in place is shown in Fig. 1. It was mounted on a cast aluminum platform and covered with a light-tight box. For experiments No. 1 to No. 4 the light source was a General Electric

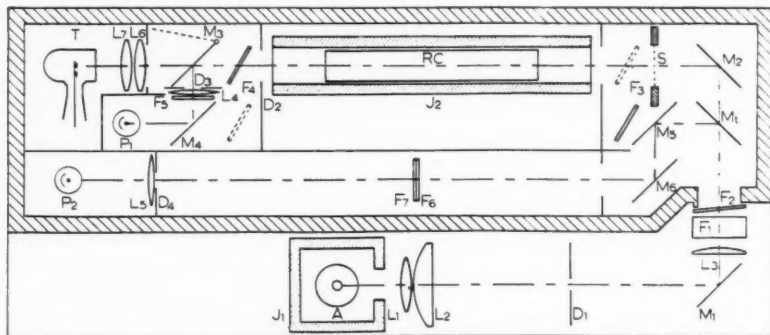


FIG. 1. Optical system.

AH-4 lamp shielded from draughts and operated from a Sorensen a-c. electronic voltage regulator. For the subsequent experiments the light source was a General Electric H-400 lamp (A) mounted inside a double-walled copper jacket (J_1) with an opening in the position shown. Cooling water was passed through the jacket.

The light from the lamp was collimated by the lenses L_1 , L_2 , L_3 , and the diaphragm D_1 . The mirror M_1 (as well as M_2 , M_3 , M_4 , M_5 , and M_6) was of the first surface aluminized type. A 2-cm. path of 2.5% aqueous cupric chloride solution (F_1) was used to remove infrared radiation. The light entered the box through the No. 3389 Corning filter (F_2) which removed wave lengths less than 4358 \AA . This filter was mounted at a slight angle to prevent the reflection back through the cell of light reflected from the windows of the reaction cell and jacket J_2 .

The parallel beam was split into a photolysis and photometric beam and a reference beam by the plane polished glass sheet M_t . The intensity of the reference beam was reduced by the aluminized reflection filter F_6 , which had a transmission of approximately 30%, and rendered monochromatic (4358 \AA) by the No. 5113 Corning filter F_7 . The use of the reflection filter avoided changes in the transmission of the filter F_7 owing to the rise in temperature brought about by the absorption of wave lengths greater than 4358 \AA .

The exposure time was controlled by the externally operated shutter S. The intensity of the light incident on the cell could be varied by a factor of approximately 20 without changing the intensity falling on the photocell P_1 by more than a few per cent. This was accomplished by changing the positions of the filters F_3 and F_4 to the "dotted" positions by an external control. These filters were of the partially aluminized reflection type and had transmissions of approximately 5%; they were mounted at an angle to throw the reflected portion of the light against the blackened internal walls of the apparatus. By rotating the mirror M_3 into the "dotted" position the light transmitted through the reaction cell could be made to fall on the vacuum thermocouple T.

The No. 5113 Corning filter F_5 was placed behind rather than in front of the reaction cell in order to gain a factor of approximately four in the intensity of 4358 Å. Although the light passing through the reaction cell was not monochromatic the only line other than 4358 Å which would be subject to absorption under the conditions used was that at 4916 Å. Because of its low relative intensity and absorption coefficient it caused an error of less than 1% in the average rate of light absorption \bar{I}_a in the most unfavorable case.

The Photocell Circuit

The relative intensities of the beams reaching the two GL-935 photocells P_1 and P_2 were measured with the bridge circuit shown in Fig. 2. The resistor r_1 was made in the

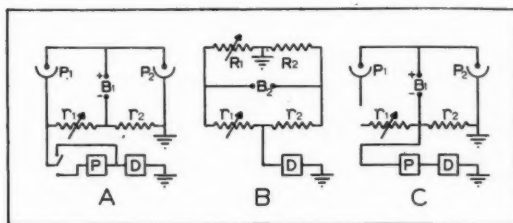


FIG. 2. Schematic diagram of the photometer circuit.

form of a five-decade unit with steps of 10^4 to 10^8 ohms; r_2 was a single decade unit with steps of 10^8 ohms. The individual resistors in each decade were accurate to 5%; they were mounted on ceramic tap switches and contained in a shielded desiccated box. R_1 and R_2 were precision General Radio decade resistors. The null detector D was a Leeds and Northrup type 7673 electrometer tube amplifier adjusted for "zero" grid current. Potentials could be measured with a potentiometer P.

The ratio of the two photocurrents, in terms of r_1 and r_2 , was measured with the circuit of Fig. 2 A. The small 45-volt battery B_1 was contained inside the shielded photocell compartment. The exact ratio of r_1 to r_2 was obtained with circuit 2 B; a separate 45-volt battery B_2 was used for this purpose. The photocurrent from P_2 could be measured in terms of the potential drop across r_2 using the circuit 2 C. With r_2 shorted out the photocurrent from P_1 could be measured in a similar way using circuit 2 A.

Great care was taken in insulating, shielding, and grounding the various parts of the circuit. With these precautions the dark currents were of the order of 10^{-18} amp. While these were about 10 times the limiting grid current of the detector they were small enough to be neglected. In a typical experiment the voltage drops across r_1 and r_2 were of the order of 4 volts, while the sensitivity of the detector was of the order of 0.1 mv.

Correction for Reflection, Absorption, and Scattering

The apparent fraction of light transmitted by chlorine in the reaction cell is given by the expression

$$(i) \quad \alpha_a = (r_2/r_1)_t / (r_2/r_1)_0 = S_t/S_0,$$

in which the subscripts t and 0 indicate the presence and absence of chlorine, respectively. Because of the reflection, absorption, and scattering of light by the windows of the cell and jacket α_a cannot be equated to the expression 10^{-KCL} , in which K is the extinction coefficient of chlorine, C is its concentration, and L is the internal path length of the cell. It has been shown elsewhere (3) that changes in chlorine concentration can be calculated accurately by means of the expression

$$(ii) \quad d(\text{Cl}_2) = (1/K_a L) d \log_{10}(S_0/S_t),$$

in which the apparent differential extinction coefficient K_a is given by the expression

$$(iii) \quad K_a = K(1 + 2\delta\alpha_a^2).$$

The quantity δ is characteristic of the particular experimental arrangement; in the present instance its value was found to be 0.0427. While the value of K_a is a function of the chlorine concentration the fractional change in chlorine concentration in any particular experiment was small enough to permit the use of a single value of K_a throughout that experiment. The true extinction coefficient of chlorine for 4358 Å was found to be $1.51 \times 10^3 \text{ cm}^2 \text{ mole}^{-1} \pm 0.5\%$ at 25°C.; its temperature coefficient was given by $K_{50.4^\circ}/K_{25.0^\circ} = 1.0215 \pm 0.0007$ (3).

If $(1-\alpha)$ is appreciably less than unity and the reaction cell is filled with a reasonably homogeneous beam the *local* rate of light absorption I_a can be equated to the *average* rate of light absorption \bar{I}_a (6). Ideally,

$$(iv) \quad \bar{I}_a = (1/L)I_0(1-\alpha).$$

To take account of the factors considered above it is convenient to express \bar{I}_a in the form

$$(v) \quad \bar{I}_a = (1/L)(I_0)_a(1-\alpha_a),$$

in which the apparent incident light intensity (einsteins $\text{cm}^{-2} \text{ sec}^{-1}$) is given by

$$(vi) \quad (I_0)_a = P_0 f / A,$$

P_0 is the response of the thermopile with the cell empty (einsteins sec^{-1}), A is the cross-sectional area of the reaction cell, and f is a correction factor.

In applying equations (ii) and (iii) it is not necessary to presuppose ideal optics or to make individual calculations of the amount of light reflected (R) and transmitted (T) by the windows. However, in evaluating \bar{I}_a these quantities appear explicitly in the expression for f ,

$$(vii) \quad f = (1-R^2)(1-\delta\alpha^2)/[T(1-\alpha R)(1+\delta\alpha)].$$

R was calculated to be 0.15, from refractive index measurements as was done by Hunt and Hill (4); T was found experimentally to be 0.840. Values of f for $\alpha = 0.50, 0.75$, and 1.00 were 1.21, 1.24, and 1.26, respectively.

RESULTS AND THEIR INTERPRETATION

The over-all reaction $\text{RH}_2\text{Cl} + \text{Cl}_2 = \text{RHCl}_2 + \text{HCl}$ was studied at 10°, 25°, and 50° C. It was evident from the dependence of the rates on light intensity that both first and second order chain termination were important. The other main reactions were assumed to be



It can be shown that, regardless of the particular nature of the chain termination steps, the rate of consumption of chlorine will be given by the expression

$$(viii) \quad -d(\text{Cl}_2)/dt = \mathcal{B} \{ (1 + \mathcal{A}\bar{I}_a)^{\frac{1}{2}} - 1 \}.$$

In the most general case, involving inhibition by one of the products or further chlorination of RHCl_2 , the terms \mathcal{A} and \mathcal{B} will be mixed functions of rate constants and concentrations. Nevertheless, numerical values of \mathcal{A} and \mathcal{B} can be obtained for the conditions obtaining when an experiment is interrupted and the light intensity changed. At the point of interruption,

$$(ix) \quad \mathcal{A} = 4r(r-1)(\lambda-r)/\bar{I}_a''(r^2-\lambda)^2,$$

in which $(-d(\text{Cl}_2)/dt)' / (-d(\text{Cl}_2)/dt)'' = r$ and $\bar{I}_a' / \bar{I}_a'' = \lambda$. Thus from a knowledge of the rates and light intensities immediately before and immediately after a change in light intensity it is possible to study the functional forms of \mathcal{A} and \mathcal{B} .

For experiments at low light intensities it is convenient to write (viii) in the form

$$(x) \quad -d(\text{Cl}_2)/dt = \frac{1}{2} \mathcal{A} \mathcal{B} \bar{I}_a T_1,$$

in which T_1 is a small correction term which approaches unity as \bar{I}_a tends to zero, whose value is given by

$$(xi) \quad T_1 = 2 \{ (1 + \mathcal{A}\bar{I}_a)^{\frac{1}{2}} - 1 \} / \mathcal{A}\bar{I}_a.$$

For experiments at high light intensities (viii) takes the form

$$(xii) \quad -d(\text{Cl}_2)/dt = \mathcal{B} \mathcal{A}^{\frac{1}{2}} \bar{I}_a^{\frac{1}{2}} T_2,$$

in which the T_2 is a small correction term which approaches unity at high light intensities, whose value is given by

$$(xiii) \quad T_2 = \frac{1}{2} \mathcal{A}^{\frac{1}{2}} \bar{I}_a^{\frac{1}{2}} T_1.$$

Since the correction terms can always be evaluated from light-interrupted experiments it is possible to investigate the nature of both the limiting low light intensity and the limiting high light intensity rate equations. In principal this permits the precise nature of each of the two types of chain termination to be studied independently.

Experiments at Low Light Intensities

Data obtained at 25° C. for these experiments are given in Table I. In most cases subsequent measurements were made using a light intensity 20.5 times as large as that indicated in the table, which permitted the evaluation of \mathcal{A} from (ix) and T_1 from (xi). The subscripts i and f refer to the initial and final conditions of the low light intensity portion of the experiment.

TABLE I
 EXPERIMENTS AT LOW LIGHT INTENSITIES, 25° C.*

Run	I_{a_i} $\times 10^{12}$	$(Cl_2)_i$ $\times 10^7$	$(RH_2Cl)_i$ $\times 10^7$	$(HCl)_i$ $\times 10^7$	(P) $\times 10^7$	Rate _i $\times 10^9$	$\frac{I_{a_i}}{I_{a_f}}$	$\frac{(Cl_2)_i}{(Cl_2)_f}$	$\frac{(RH_2Cl)_i}{(RH_2Cl)_f}$	Rate _f	T_1
1	6.37	67.0	4.14	0	71.1	3.77	1.018	1.026	1.73	1.00	0.96
2	6.17	64.6	4.12	4.98	73.7	3.92	1.019	1.027	1.78	1.03	0.95
3	6.14	66.0	4.12	38.0	108.1	3.06	1.011	1.016	1.36	1.00	0.95
4	6.61	78.3	4.13	0	82.4	5.30	1.017	1.024	1.81	1.11	0.96
5	6.64	73.4	6.23	0	79.6	7.40	1.016	1.023	1.44	1.10	0.90
6	30.0	74.2	4.27	0	78.5	19.3	1.015	1.022	1.61	1.12	0.86
7	30.0	74.2	8.14	0	82.3	35.7	1.024	1.034	1.42	1.10	0.90
8	28.8	74.4	4.24	0	78.6	20.6	1.013	1.019	1.49	1.06	—
9a	109	9.44	9.37	0	18.8	33.3	1.255	1.265	1.27	1.66	—
14	16.9	42.5	4.19	0	46.7	14.0	1.033	1.038	1.64	1.17	0.79
15a	56.0	23.1	9.11	0	32.2	68.0	1.063	1.070	1.20	1.23	—

*The units used are moles, cm.³, einsteins, minutes; (P) is the total "pressure" in moles cm.⁻³; the subscripts i and f refer to initial and final conditions in the low light intensity portion of the experiment.

Except in the case of experiments 9a and 15a, it is evident from a comparison of columns 10 and 11 that a considerable change in (RH_2Cl) during an experiment has relatively little effect on the rate despite the fact that the initial rates (column 7) appear to be proportional to the initial concentrations of RH_2Cl . Compare, for example, Expt. 4 with Expt. 5, or Expt. 6 with Expt. 7. These observations suggested that the quantity \mathcal{AB} in equation (x) should be proportional to $(RH_2Cl)_i$ or to $\{(RH_2Cl) + (RHCl_2)\}$, at least to a first approximation.

It is evident from the initial rate of Expt. 3 that the reaction is inhibited by hydrogen chloride, presumably through the reaction



This would also account for the large change in rate during the course of Expts. 9a and 15a.

A third effect apparent from the results of Table I is that of total pressure. If the initial rate of Expt. 9a is "corrected" to the initial conditions of Expt. 7, assuming the rate to be directly proportional to \bar{I}_a and to $(RH_2Cl)_i$, the resulting "rate" is less than that for Expt. 7 by a factor of 4.5. This is almost identical to the ratio of the total pressures in the two experiments.

The above observations suggest that the quantity \mathcal{AB} in equation (x) should be proportional to

$$\{(RH_2Cl) + (RHCl_2)\} (P) / [1 + D(HCl)/(Cl_2)].$$

If it is assumed that the rate of removal of atomic chlorine by the first order termination process, which may be referred to as [5], is given by

$$(xiv) \quad \{-d(Cl)/dt\}_{\text{term.}} = k_a(Cl)(RH_2Cl) / \{(RH_2Cl) + (RHCl_2)\} (P),$$

and if the other elementary reactions involved are [1], [2], [3], and [4], the following rate equation is derived:

$$(xv) \quad -d(Cl_2)/dt = 2k_2\bar{I}_a\{(RH_2Cl) + (RHCl_2)\} (P) T_1 / [k_a\{1 + (k_4/k_3)(HCl)/(Cl_2)\}].$$

The unusual form of (xv) arises, of course, from the assumption that the first order chain termination process is given by (xiv). This expression would obtain if chlorine atoms diffuse to the walls at a rate proportional to $1/P$ and there react with adsorbed

RH_2Cl to form a product which does not leave the walls as a radical. The further assumption is that both RHCl_2 and RH_2Cl are adsorbed on the walls and that the fraction covered by RH_2Cl is proportional to $(\text{RH}_2\text{Cl})/\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\}$. The last assumption is not unreasonable since the two molecules are similar in many respects and the ratio of their equilibrium vapor pressures at room temperature (0.8) does not differ greatly from unity.

If the rate of removal of atomic chlorine from the gas phase were determined simply by the rate of diffusion to the walls, and were independent of the gas phase concentrations of RH_2Cl and RHCl_2 , except insofar as they affect the total pressure (P), then,

$$\text{(xvi)} \quad \{-d(\text{Cl})/dt\}_{\text{term.}} = k_b(\text{Cl})/(P),$$

and

$$\text{(xvii)} \quad -d(\text{Cl}_2)/dt = 2k_2\bar{I}_a(\text{RH}_2\text{Cl})(P)T_1/[k_b\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}].$$

The decision between (xv) and (xvii) was based on the linearity of plots, vs. time, of the functions ϕ_a and ϕ_b , viz.,

$$\text{(xviii)} \quad \phi_a = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{2\bar{I}_a\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\}(P)T_1} = (k_2/k_a)t,$$

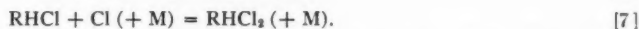
$$\text{(xix)} \quad \phi_b = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{2\bar{I}_a(\text{RH}_2\text{Cl})(P)T_1} = (k_2/k_b)t.$$

The values of k_4/k_3 used in the above expressions were 1.2, 2.47, and 5.0 for 10°, 25°, and 50° C., respectively; the method used to obtain them will be described below. Whereas good linear plots were obtained for ϕ_a , those for ϕ_b were invariably curved. In every case the evidence was in favor of (xv) as the limiting low light intensity rate equation. It should be mentioned that first order removal of RHCl radicals from the gas phase was also considered, but the corresponding rate equation was quite inconsistent with the observed dependence of the rate on (RH_2Cl) and (HCl) .

It must be admitted that the suggested mechanism of first order termination is a sufficient but not a necessary condition for the observed rate equation (xv). It has been suggested by a reviewer that an equation similar to (xiv) might obtain if impurities were present, although it would be difficult to account for the quantity (P) in that case.

Experiments at High Light Intensities

At high light intensities the observed rates were strongly dependent on (RH_2Cl) and the reaction was inhibited by HCl . While this eliminated the bimolecular combination of RHCl radicals as an important chain termination step, it left some uncertainty as to whether the main termination reaction was [6] or [7],



The decision between the two reactions was based on the linearity of plots, vs. time, of the functions ϕ_c and ϕ_d :

$$\text{(xx)} \quad \phi_c = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{\bar{I}_a^{1/2}(\text{RH}_2\text{Cl})T_2} = \frac{k_2}{k_6^{1/2}(\text{M})^{1/2}}t,$$

$$(xxi) \quad \phi_d = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\} d(\text{Cl}_2)}{\bar{I}_a^{1/2} (\text{Cl}_2)^{1/2} (\text{RH}_2\text{Cl})^{1/2} T_2} = \frac{(k_2 k_3)^{1/2}}{(k_7(M))^{1/2}} t.$$

For experiments carried out at 50° C. plots of ϕ_c vs. t remained linear until 60 to 70% of the RH_2Cl was consumed; at 10° C. and 25° C. the duration of the linear portion of the curve was even greater. On the other hand, plots of ϕ_d vs. t were invariably curved. There is little doubt, therefore, that [6] is the predominant second order termination reaction. At high conversions some curvature of the ϕ_c plot is brought about because of the subsequent chlorination of RHCl_2 .

From the slopes of the curves of ϕ_c vs. t for the various experiments it was evident that a third body mechanism applied to reaction [6], and that within the experimental accuracy (M) was equal to $(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)$. It is not surprising that these two heavy and relatively complex molecules should be more efficient third bodies than either Cl_2 or HCl .

Values of $k_2/k_6^{1/2}$, calculated from (xx), and of k_2/k_a , calculated from (xviii), are given in Table II. The final calculations were, of course, done after the limiting low light intensity and limiting high light intensity mechanisms had been established.

TABLE II
RATE CONSTANTS FOR LOW AND HIGH LIGHT INTENSITY MECHANISMS

Run	Temp., ° C.	k_2/k_a ,	$k_2/k_6^{1/2}$, min. ^{-1/2}	(RH ₂ Cl) _i *	(Cl ₂) _i	(HCl) _i	I_0/L^\dagger × 10 ¹¹
		cm. ⁶ mole ⁻² × 10 ⁻¹⁴		mole cm. ⁻³ × 10 ⁷			
1	25.0	1.15	26.1	4.14	67.0	0	1.37
2	25.0	1.15	26.2	4.12	64.6	4.98	1.37
3	25.0	1.13	26.8	4.12	66.0	38.0	1.36
4	25.0	1.30	26.7	4.13	78.3	0	1.33
5	25.0	1.15	27.2	6.23	73.4	0	1.32
6	25.0	0.98	26.6	4.27	74.2	0	5.98
7	25.0	1.02	27.6	8.14	74.2	0	5.95
8	25.0	1.15	27.8	4.24	74.4	0	5.75
9a	25.0	1.10	—	9.37	9.44	0	125
9b	50.4	2.80	—	7.39	7.46	1.98	125
9c	25.0	1.20	—	5.49	5.56	2.88	125
10	50.4	3.0	50.1	4.23	73.2	0	2.84
11	50.4	3.15	49.0	4.35	72.8	0	2.82
12	50.4	3.25	54.7	7.64	73.0	0	1.86
13	50.4	3.5	54.5	6.42	73.4	0	1.86
14	25.0	2.7	23.2	4.14	42.5	0	5.07
15a	25.0	1.7	—	9.11	23.1	0	28.0
15b	50.4	2.9	—	7.57	21.6	1.54	28.0
16	10.0	1.4	16.23	4.25	73.1	0	5.03
17	10.0	1.15	16.36	4.24	73.0	0	5.01
18	10.0	1.50	16.36	4.18	72.9	0	4.97

* Made up of RH_2Cl (97%) and RHCl_2 (3%).

† Einsteins cm.⁻² minutes⁻¹. Values are for low light intensity part of the run. Values for high light intensity part were 20.5 times as large. High I_0 used throughout runs 9 and 15.

The value of k_4/k_3 at 25° C. (2.47) was obtained by arbitrarily setting $k_2/k_6^{1/2}$ at the value 26.8 for the high light intensity part of run 3. The value of k_4/k_3 at 50° C. (5.0) was obtained by assuming the value 2.80 for k_2/k_a in run 9b; the value at 10° C. was obtained by extrapolation of an Arrhenius plot through the two other numbers. The activation energy difference $E_4 - E_3$ obtained from the two higher temperatures is admittedly crude. Assuming an error of 10% in the 25° value and 20% in the 50.4° value, $E_4 - E_3 = 5.4 \pm 1.6$ kcal. per mole, and $\log(A_4/A_3) = 4.4 \pm 1.2$. Actually, the

correction term $\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}$ contributed very little except for runs 9 and 15.

From a plot of $\log(k_2/k_6^{1/2})$ vs. $1/T$ the activation energy difference $E_2 - \frac{1}{2}E_6$ was found to be 5.2 ± 0.3 kcal. per mole; this is essentially the activation energy of reaction [2]. The quantity $\log(A_2/A_6^{1/2})$ was 4.3 ± 0.2 .^{*} The values of $k_2/k_6^{1/2}$ are more reproducible than those of k_2/k_a , as might be expected.

DISCUSSION

It is evident from the present work that the mechanism for the photochlorination of monochloromethyl chloroformate (RH_2Cl) is similar to that for the photochlorination of methyl chloroformate (RH_3) (2). In each case the first and second order chain termination steps involve atomic chlorine.[†] In contrast to the present results, HCl did not appear to inhibit the chlorination of RH_3 .

The rate constant for hydrogen abstraction from RH_2Cl by reaction [2] is somewhat smaller than that for the corresponding abstraction from RH_3 ,



Brandy and Le Roy (2) did not interpret the bimolecular combination of atomic chlorine as a third body process, but values of $k_2'/k_6^{1/2}$ in the range 37 to 58 minutes^{-1/2} can be calculated from their data on the assumption that RH_3 was the third body; at the same temperature (25° C.) $k_2/k_6^{1/2}$ was 26.8 minutes^{-1/2}.

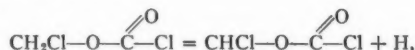
Assuming that E_2 is 5.2 kcal. per mole, the effect of temperature on k_2/k_a suggests that E_a is probably less than this. Such a result would be expected if the first order termination process were entirely diffusion controlled. This, however, is not the case, and although the results have indicated a rather detailed picture of the process it is not considered worth while at this time to discuss the theoretical aspects of k_a .

It is evident from the mechanism that

$$(xxii) \quad (\text{Cl})/(\text{RHCl}) = (k_3/k_2) \times \{(\text{Cl}_2)/(\text{RH}_2\text{Cl})\} \times \{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}.$$

Also, reaction [7] was much less important than [6], if it occurred at all, despite the fact that a third body is required for [6] and would probably not be required for [7]. It seems safe to conclude that (Cl) must have been at least 10 times as large as (RHCl) even when the inhibition term was negligible and $(\text{Cl}_2)/(\text{RH}_2\text{Cl})$ was less than 10. The internal evidence is, therefore, that $k_3 > k_2$, or $A_3e^{-E_3/RT} > A_2e^{-E_2/RT}$. A consideration of the factors contributing to the entropy of activation suggests that A_3 is likely to be less than A_2 and hence E_3 less than E_2 .

Assuming, conservatively, that $E_3 = 2.6 \pm 2.6$ kcal. per mole, that $E_4 - E_3 = 5.4 \pm 1.6$ kcal. per mole, and that the bond dissociation energy in HCl is 102.57 kcal. per mole (5), it follows that the C—H bond dissociation energy in RH_2Cl , defined as the thermodynamic quantity ΔE°_{298} for the reaction



is 99.8 ± 4.5 kcal. per mole. In this respect the hydrogen atoms in monochloromethyl chloroformate closely resemble the primary hydrogen atoms of aliphatic hydrocarbons.

^{*}For $A_2/A_6^{1/2}$ expressed in sec.^{-1/2}.

[†]In Ref. 2, p. 1053, line 27, "5a" should read "5b".

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NUCLEAR MAGNETIC RESONANCE MEASUREMENTS IN SOLUTIONS OF ACETYLACETONE

THE EFFECT OF SOLVENT INTERACTIONS ON THE TAUTOMERIC EQUILIBRIUM¹

L. W. REEVES²

ABSTRACT

A modified assignment of the PMR signals in acetylacetone is confirmed. The changes in intensity of selected signals with temperature are used to calculate an enthalpy of conversion of 2700 ± 100 cal. between keto and enol forms in pure acetylacetone.

Interactions, which perturb the equilibrium between the tautomeric forms in dilute solution by formation of solution complexes, are studied by observing dilution chemical shifts in various solvents. The ratio of keto to enol forms is estimated from measurements of signal intensities at several dilutions in each solvent. The deviations from the correlations of Bernstein and Powling (5) between solvent dielectric constant and molar volume, and the position of the tautomeric equilibrium in dilute solutions, have been used as a criterion of solvent interaction. They are consistent with the present measurements.

Typical basic, acidic, amphoteric, and neutral solvents have been chosen to investigate possible types of interaction. Cyclohexane and acetic acid do not perturb the equilibrium by any interactions. Triethylamine forms a hydrogen bonded complex through the enolic —OH group and the nitrogen lone pair, thus converting acetylacetone completely to enol form. Pyrrole forms a weakly hydrogen bonded complex through the carbonyl oxygens of the keto form. Freezing diagrams in the interacting systems are consistent with the complexes suggested by the PMR measurements.

INTRODUCTION

Several studies of tautomerism have been made since the early work of Meyer and co-workers (15) in order to correlate the structure of the molecules and the solvents used with the position of the equilibrium (8, 10, 16). The standard enthalpy change in a tautomeric conversion depends to a certain extent on the structure of the molecule and also on the solvent environment.

Bernstein and Powling (5) were able to show that the displacement of the keto-enol equilibrium in dilute non-polar or slightly polar solutions is determined by changes in dielectric constant of the medium. The Kirkwood-Onsager relation (13, 17) with empirical extensions is able to correlate the position of equilibrium even in polar solvents such as ethers or carboxylic acids.

This and similar studies were made using a spectroscopic method of analysis, and are therefore limited to dilute solution. The influence of strongly interacting solvents is however manifest at high concentrations of the keto-enol system.

The enol form is stabilized in tautomeric systems which can form an intramolecular hydrogen bond. The exchange of the hydrogen bonded proton from one oxygen to another is a contributing factor to such stabilization (23). In view of the importance of this hydrogen bond and the appearance of NMR as a sensitive tool in the study of hydrogen bonding (1, 20, 24, 7, 18), it was thought advantageous at this time to pursue this particular aspect in acetylacetone. Typical acidic, basic, amphoteric, and non-polar solvents have been chosen.

The proton resonance in two keto-enol systems has been discussed in a brief note by Jarrett, Sadler, and Shoolery (12) and this was followed by some criticism (6) based, however, on inferior spectra.

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EXPERIMENTAL

Analytical grade acetylacetone was fractionally distilled under reduced pressures, and the selected middle fraction boiled at 139.1° C. (760 mm.). Pyrrole was also distilled under reduced pressures. The brown color which appears in this compound after it has been left for a few days was always removed on a silica gel column. NMR measurements were identical whether the compound was freshly distilled or not. Cyclohexane was the research grade available commercially, and C.P. acetic acid was refluxed, then fractionally distilled with acetic anhydride in order to remove any water.

The magnetic resonance of the proton was detected on a Varian V-4300 NMR spectrometer, operating at 40 Mc./s. Chemical shifts were measured by superimposing an audio-frequency, and using the side bands which develop to determine the chemical shifts between two signals in cycles per second (1). The resonance signals were measured from an internal standard because an equilibrium system was being investigated, the magnetic susceptibility of one component of which was difficult to estimate. The large changes in chemical shift accompanying the rupture and formation of hydrogen bonds made a knowledge of absolute chemical shifts unnecessary (4, 20) in the present study.

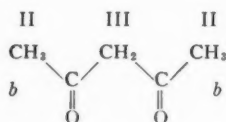
The samples were contained in 5-mm. glass tubes, which were arranged to spin in the magnetic field. When the effect of temperature was studied a modification of the apparatus of Bernstein, Schneider, and Pople was utilized, permitting simultaneous heating and spinning of the sample (2).

Intensity measurements were generally obtained from the $-\text{CH}=\text{}$ and $-\text{CH}_2$ groups in the enol and keto forms respectively. The enolic $-\text{OH}$ was considerably broadened in almost all solutions but was equal in intensity to the $-\text{CH}=\text{}$ group in the pure compound. These intensity measurements were made under conditions of high resolution, sweep rates being less than 10 milligauss per minute. The radio-frequency power was kept well below saturation and above the threshold at which signal intensity becomes proportional to proton concentration. Experimental tests of these conditions were always verified.

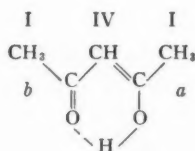
RESULTS

The spectrum of pure acetylacetone under conditions of high resolution confirms the results of Jarrett, Sadler, and Shoolery (12). The various signals are similarly assigned except for the methyl groups and appear in Fig. 1. These peaks are shown with varying gain and at a sweep rate of 10 μ gauss/minute; intermediate regions are omitted. Intensities in a continuously run spectrum indicate the signals to be: V, $-\text{OH}$; IV, $-\text{CH}=\text{}$; III, $-\text{CH}_2-$; II, CH_3- (keto form); and I, CH_3- (enol form) from low to high field respectively.

The methyl signals I and II in Fig. 1, however, are difficult to assign accurately on the basis of intensities, since they are separated by only 7 c./s. The two possible assignments are:



Keto

V
Enol

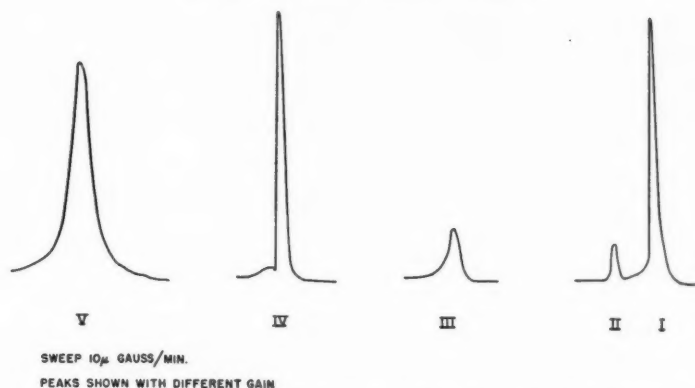


FIG. 1. PMR spectrum of pure acetylacetone at 25° C. Signals shown at different gain with intermediate regions omitted.

1. Methyl group *a* is unique, and methyl groups *b* are identical. The signal I in Fig. 1 is then due to methyl groups *b* and signal II to methyl group *a*.

2. The enol methyl groups give signal I and keto methyl groups give signal II.

A temperature increase favors more keto form and thus the variation of intensity with temperature enables the signal to be correctly determined. Signal II in Fig. 1 was found to increase in intensity between 25° and 110° C. and therefore it must belong to the keto form. The correct assignment is therefore assignment 2 above and subsequently signals I and II will be referred to as the enolic and keto methyl groups respectively.

The internal standard used in almost all measurements was the enolic methyl group since it occurs at highest field; all chemical shifts at lower field are denoted by a positive number. On this basis chemical shifts for the five signals are given in Table I to the nearest cycle at 40 Mc./s.

The enolic —OH group is at lower field than any other proton signal yet found. Approximate half widths for these signals at a sweep rate of 10 milligauss per minute show interesting differences. The methyl groups and the enolic —CH= are narrow with half widths of approximately 0.12 milligauss* but the corresponding figures for the enolic

TABLE I
CHEMICAL SHIFTS IN PURE ACETYLACETONE AT 40 Mc./s.

Signal	Refer to Fig. 1	Chemical shift, c./s. at 40 Mc./s.	P.p.m.
Enol CH ₃ —	I	0	0
Keto CH ₃ —	II	7	0.17
Keto —CH ₂ —	III	66	1.65
Enol —CH=	IV	143	3.58
Enol —OH	V	543	13.58

—OH group and the —CH₂— group are ~ 0.42 μgauss and ~ 0.28 μgauss respectively. Solvents invariably affected the broadness of the —OH signal, in some cases rendering detection of the signal impossible at maximum sensitivity, even in solutions of mole fraction 0.3.

*The resolving power is only slightly better than this figure.

Careful and repeated measurements of the intensity of the —OH , —CH= , and $\text{—CH}_2\text{—}$ signals at varying sweep rates and r-f. power showed the presence of $18.6 \pm 0.6\%$ keto form in the mixture. (The maximum deviation from the mean of five determinations is indicated in the error.) Table II summarizes the results obtained by

TABLE II
ESTIMATION OF THE EQUILIBRIUM MIXTURE IN ACETYLACETONE AT
ROOM TEMPERATURE (25°C .)

	Reference	Method	% Keto	% Enol
Jarrett, Sadler, and Shoolery	(10)	PMR	15	85
Bhar	(15)	PMR	24	76
Present work		PMR	18.6	81.4
Meyer <i>et al.</i>	(1)	Bromine titration	24	76

other workers. The disadvantage of the chemical method in disturbing the equilibrium is well known and the agreement obtained by Bhar with the chemical method is based on inferior spectra showing pronounced tails to all peaks. A resolving power in the region of a few tenths of a milligauss claimed by Shoolery *et al.*, at 30 Mc./s., will be slightly improved at the higher frequency of 40 Mc./s. with the same field stabilization in the present measurements. In addition the improvements inherent in the use of a high response slow speed recorder (Varian G10) with the slow sweep of 10 milligauss per minute or less make the present measurements at least comparable to those of Shoolery *et al.* The intensity measurement of two signals of differing half widths has certain disadvantages, particularly when one of these signals has a half width in the region of the instrumental resolving power. Both the —OH (enol) and $\text{—CH}_2\text{—}$ (keto) are considerably broader than the —CH= (enol) resonance but in solvents the —OH resonance became unsuitable. It is reassuring, therefore, that in the pure acetylacetone the analysis is independent of whether the (—OH) or the (—CH=) group is used for intensity measurements. The intensities of the enolic —CH= and the keto $\text{—CH}_2\text{—}$ were measured at various temperatures between -16°C . and 116°C . in order to determine the position of the equilibrium at these temperatures. The temperature variation of the equilibrium constant was used to compute the enthalpy of conversion between the two forms. Equilibrium was established at any temperature after a period of 2 hours; the temperature control possible was $\pm 0.5^\circ\text{C}$. The values of $\log(c_1/c_2)$ vs. $1/T^\circ\text{K}$. are plotted in Fig. 2, where c_1 and c_2 are the mole fractions of keto and enol at equilibrium respectively. The value of $-\Delta H$ obtained was 2705 ± 100 cal. from the graph. The error indicated is the maximum and minimum slope through experimental points.

Solutions of Acetylacetone in Pyrrole

The proton magnetic resonance spectrum of pyrrole is shown in Fig. 3. This should be a typical A_2B_2 case in the terminology of Bernstein, Schneider, and Pople (3, 4), but it shows a much simpler form than might be expected from 16 energy levels so arranged (4). The nature of the spectrum may be resolved by dilution in cyclohexane, which causes a chemical shift to occur between the components of the spectrum. It can be seen from Fig. 4 that pure pyrrole consists of two overlapping quartettes, which separate on dilution in cyclohexane.

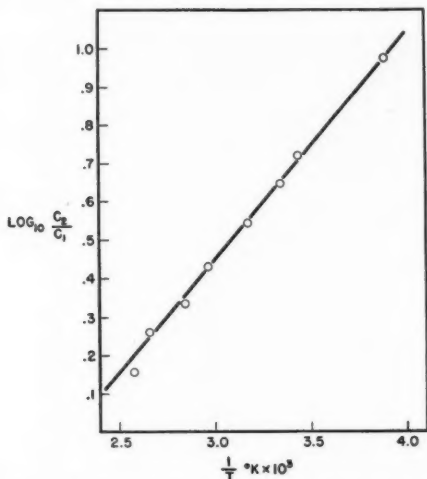


FIG. 2. The variation in concentration of the tautomeric forms in pure acetylacetone with temperature from intensity measurements of resonance signals.

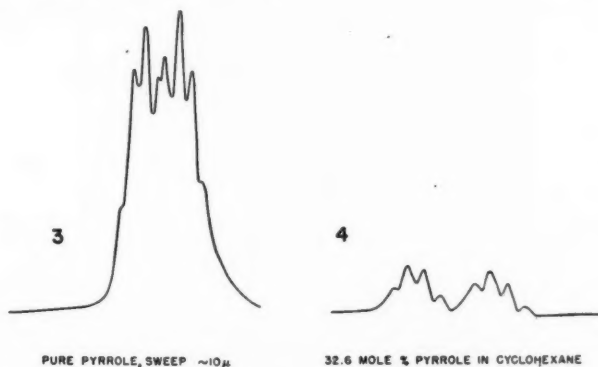


FIG. 3. The PMR spectrum of pure pyrrole, sweep rate $\sim 10 \mu\text{gauss/minute}$.

FIG. 4. PMR spectrum of a solution of pyrrole in cyclohexane.

It will be convenient to speak of the high field and low field signals to distinguish them. The chemical shift between these two signals in pure pyrrole was found to be 7.5 c./s. at 40 Mc./s. (0.19 p.p.m.) and the J coupling constant 2 c./s. At infinite dilution in cyclohexane the pyrrole signals separate to give a modified chemical shift of 11.5 c./s. at 40 Mc./s. (0.29 p.p.m.). The volume susceptibility of pyrrole has not been recorded in the literature and its estimation from Pascal constants would be too much in error to compute an absolute chemical shift in the region of 10 c./s. The figures quoted therefore take no account of the bulk diamagnetic effects.

The proton resonance of the $-\text{NH}$ group was not generally detectable because of the broadening effect of the nitrogen quadrupole; nevertheless this signal appeared in solutions containing acetylacetone. The spectrum of such a solution is shown in Fig. 5 with a mole fraction of 0.537 acetylacetone.

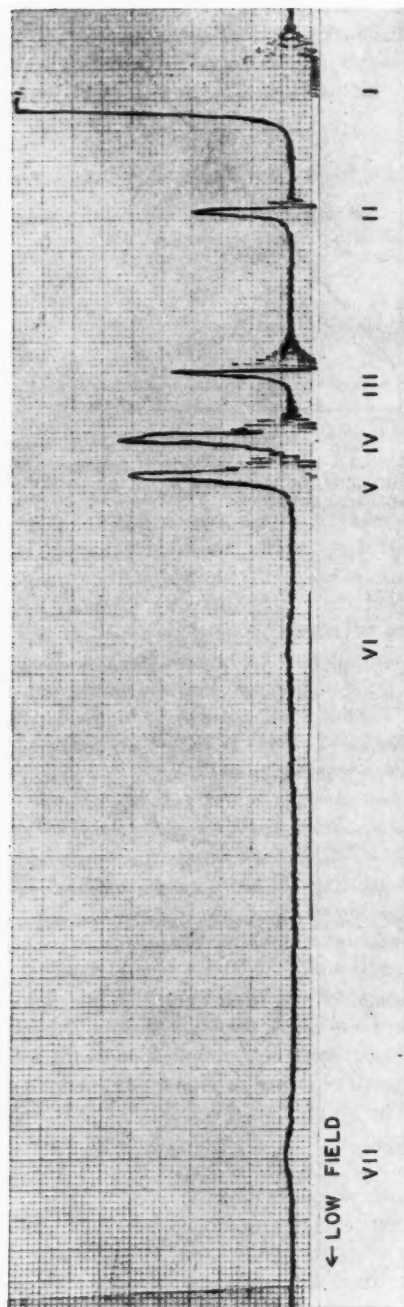


Fig. 5. PMR spectrum of acetylacetone in pyrrole at 25°C., mole fraction 0.54. Assignment of signals: I, methyl groups of acetylacetone; II, $\text{CH}_2=\text{CH}-$ group, keto form; III, $-\text{CH}=\text{CH}-$ group, enol form; IV and V, $-\text{CH}=\text{CH}-$ groups in pyrrole ring; VI, N—H group, pyrrole; and VII, $-\text{OH}$ group, enol form.

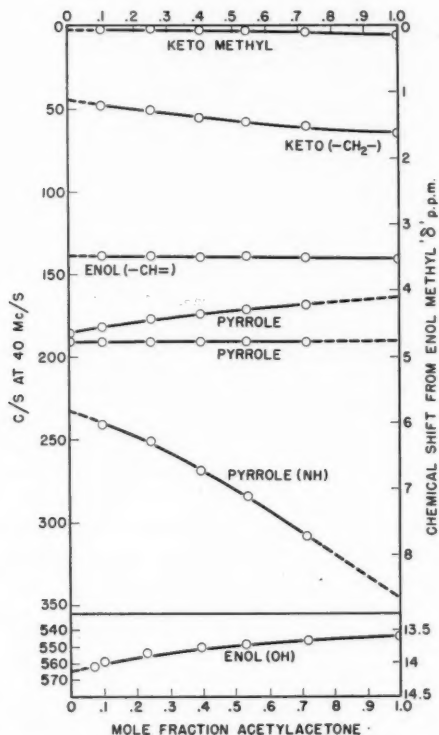


Fig. 6. Dilution chemical shifts of all signals in acetylacetone-pyrrole solutions, referred to enol methyl signal.

Fig. 6 shows the changes in chemical shift which occur at all dilutions of pyrrole in acetylacetone; the enol methyl has been used as an internal standard. The data are extrapolated to infinite dilution of pyrrole and acetylacetone in Table III.

TABLE III

INFINITE DILUTION SHIFTS IN THE ACETYLACETONE-PYRROLE SYSTEM (c./s. at 40 Mc./s.)

A. Mole fraction pyrrole = 0, isolated pyrrole molecule in an acetylacetone medium

B. Mole fraction pyrrole = 1, isolated acetylacetone molecule in pyrrole

	Enol methyl	Keto methyl	Keto $-\text{CH}_2-$	Enol $-\text{CH}=\text{}$	Pyrrole		$-\text{NH}$	Enol $-\text{OH}$
					High field signal	Low field signal		
A	0	7	66	143	167.5	193	349	543
B	0	3	47	143	188	193	235	565

Significant changes in chemical shift occur in the keto $-\text{CH}_2-$ (19 c./s.), the high field quartette in the protons of the pyrrole nucleus (20.5 c./s.), the N-H (114 c./s.), and the enolic $-\text{OH}$ group (22 c./s.). This information was extended by a study of the keto-enol equilibrium at various concentrations of pyrrole. The enolic $-\text{CH}=\text{}$ and

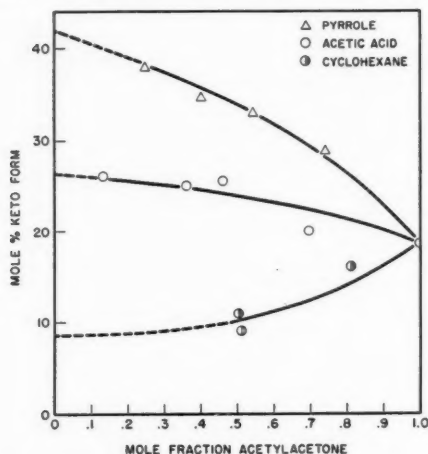


FIG. 7. The concentration dependence of tautomeric forms in pyrrole, acetic acid, and cyclohexane.

the keto $-\text{CH}_2-$ were chosen to indicate the ratio of the two forms from an intensity measurement. Averages of many traces of the spectrum at a sweep rate of ~ 10 milligauss per minute at each concentration are summarized in Fig. 7. As indicated in the spectrum shown in Fig. 5 the enolic $-\text{OH}$ group is broadened in pyrrole solutions making it unsuitable for intensity measurements.

Solutions of Acetylacetone in Cyclohexane

The changes in chemical shift from the enolic methyl were barely detectable throughout the concentration range in this solvent. Table IV summarizes the isolation shifts obtained

TABLE IV
CHEMICAL SHIFTS IN THE CYCLOHEXANE-ACETYLACETONE SYSTEM (c./s. at 40 Mc./s.)

Mole fraction acetylacetone	Enol $-\text{OH}$	Enol $-\text{CH}=\text{}$	Keto $-\text{CH}_2-$	Keto CH_3-	Enol CH_3-	Cyclohexane
0	544	141	62	5.5	0	-21
1	543	143	66	7.0	0	-22

at infinite dilution of each component and includes the position of the cyclohexane signal which moves only 1 cycle at 40 Mc./s. relative to the enol methyl signal.

Intensity measurements at different dilutions indicate that approximately 9% of the keto form is present at infinite dilution. This is shown in Fig. 7.

Solutions of Acetylacetone in Triethylamine

The investigation of these solutions for proton resonance was characterized by the lack of any signal corresponding to the keto form, even in solutions as concentrated as 0.84 mole fraction acetylacetone. The changes in chemical shift therefore correspond to interaction between acetylacetone in the enol form and triethylamine.

There is considerable broadening of the enolic $-\text{OH}$ resonance and for the first time a broader $-\text{CH}=\text{}$ signal in the enolic acetylacetone was observed (see Fig. 8). The positions of signals in Fig. 8, which shows the spectrum of a solution containing 0.66 mole fraction acetylacetone in triethylamine, are given with the assignments in Table V.

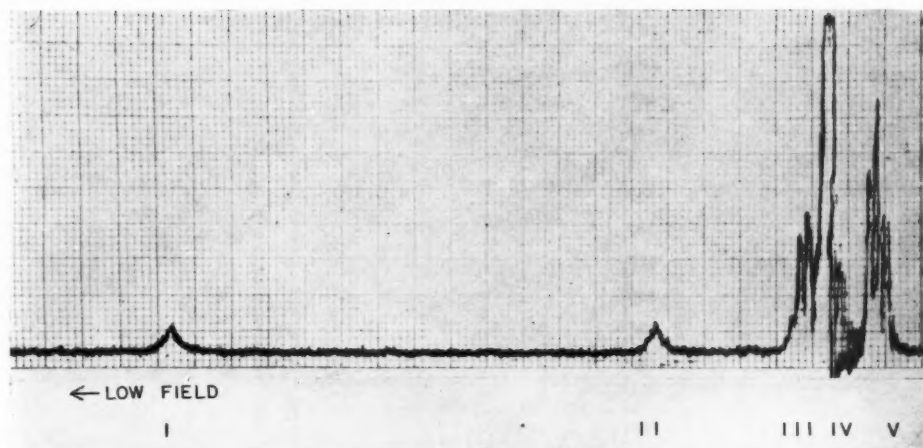


FIG. 8. PMR spectrum of acetylacetone in triethylamine, mole fraction 0.66. Assignment of signals: I, enol —OH ; II, enol —CH= ; III, triethylamine, $\text{—CH}_2\text{—}$; IV, enol methyl; and V, triethylamine $\text{CH}_3\text{—}$.

TABLE V
ASSIGNMENTS AND CHEMICAL SHIFTS OF SIGNALS IN A SOLUTION OF 0.66 MOLE FRACTION ACETYLACETONE IN TRIETHYLAMINE; SPECTRUM SHOWN IN FIG. 8

Signal	Assignment	Chemical shift from enol methyl	
		c./s.	p.p.m.
I	Enol —OH	+539	13.47
II	Enol —CH=	+143	3.58
III	Triethylamine $\text{—CH}_2\text{—}$	+20	0.50
IV	Enol $\text{CH}_3\text{—}$	0	—
V	Triethylamine $\text{CH}_3\text{—}$	-42	-1.05

The changes in chemical shift of the enol —OH group on dilution in triethylamine are shown in Fig. 9. The —OH signal moves about 250 c./s. in the concentration range down to 2 mole % acetylacetone. This is one of the largest dilution shifts so far observed. There are no significant changes in the position of other signals of these spectra as is shown in Table VI.

TABLE VI
INFINITE DILUTION SHIFTS (c./s. at 40 Mc./s.) IN THE ACETYLACETONE-TRIETHYLAMINE SYSTEM; METHYL OF ENOL FORM USED AS INTERNAL STANDARD OF CHEMICAL SHIFTS

Mole fraction acetylacetone	Enolic —OH	Enolic —CH=	Methyl groups	Triethylamine	
				Methylene	Methyl
1	543	143	0	20	-42
0	~224	143	0	20	-40

Solutions of Acetylacetone in Acetic Acid

Table VII shows the relative changes in the position of all proton signals present in mixtures of acetic acid and acetylacetone at infinite dilution of both components. The methyl of the acetic acid always coincides with the position of the enol methyl within 2 c./s.; the latter signal was again used as the internal reference signal. A considerable

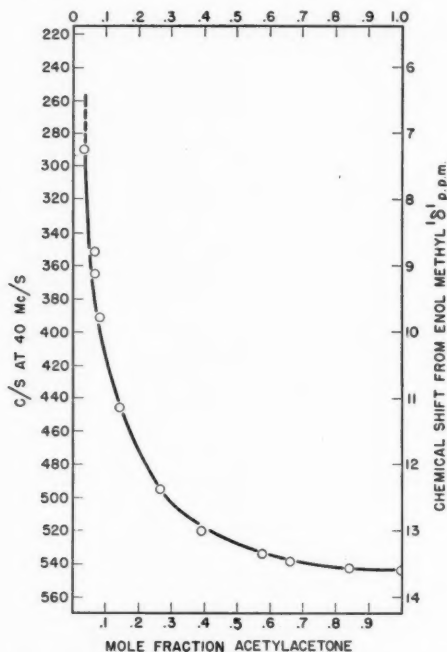


FIG. 9. Dilution chemical shift of enol —OH proton with respect to enol $\text{CH}_3\text{—}$ in solutions of acetylacetone in triethylamine.

broadening of the enolic —OH and the carboxylic —OH was observed in these solutions. At 50 mole % of each component both —OH signals had half widths > 30 c./s. at 40 Mc./s. with a sweep rate of 10 milligauss per minute. It was difficult to determine the chemical shifts of these signals at greater dilutions than this by virtue of the broadening. There were no significant changes in chemical shift, however, except the enolic —OH which moved about 10 cycles (0.25 p.p.m.).

TABLE VII
INFINITE DILUTION SHIFTS IN ACETYLACETONE - ACETIC ACID SYSTEM

Mole fraction acetylacetone	Enol —OH	Acetic acid —OH	Enol —CH=	Keto $\text{—CH}_2\text{—}$	Keto $\text{CH}_3\text{—}$	Enol $\text{CH}_3\text{—}$
1	543	~ 387	143	66	7	0
0	~ 533	387	143	66	7	0

Fig. 7 shows the position of the keto-enol equilibrium at various dilutions in acetic acid at room temperature. At infinite dilution in acetic acid the keto content is 27 mole % compared with 18.6% in the pure compound.

Freezing Diagrams in These Systems

Fig. 10 shows complex formation with both triethylamine and pyrrole. In triethylamine 1:1 and 1:2 complexes are formed, which are shown up in spite of a large difference in the melting points of the two components. Much weaker is the 2:1 pyrrole:acetylacetone complex, shown also in Fig. 10.

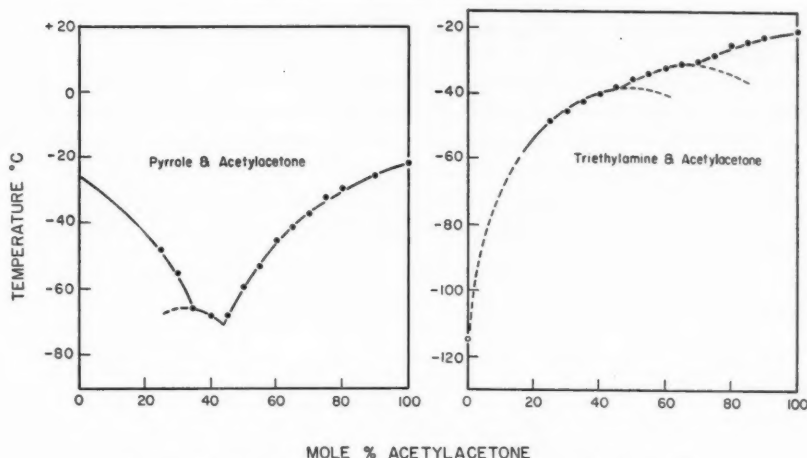


FIG. 10. Freezing diagrams in two of the systems studied by PMR.

DISCUSSION

1. Assignment of Signals in Acetylacetone

The assignment of the various signals in the present study differs from that inferred in the work of Jarrett, Sadler, and Shoolery (12). In the spectrum of 3-methyl-2,4-pentanedione they assume that the methyl group adjacent to the enolic —OH is unique. This does not agree with the results of the present experiments, which suggest an exchange of the enolic hydrogen between the two "O" atoms making the two methyl groups in the enol form identical (5). The appearance of the enolic —OH at very low field (543 c./s. at 40 Mc./s. from the enolic methyl) is indicative of a particularly stable hydrogen bond.

2. Heat of Tautomerization in Pure Acetylacetone

The enthalpy difference of 2700 cal. between the two forms of acetylacetone in the pure liquid is quite high compared to values obtained in the gas phase or dilute solutions. There is no means, however, of estimating what the enthalpy change should be in a system in which neighboring molecules participate in the equilibrium process. The present measurement indicates that the enthalpy change is considerably higher in this case, although it was not possible to extend the use of magnetic resonance to obtain enthalpies at low concentrations because of loss in intensity of the signals.

3. Criterion of Solvent Interaction with Acetylacetone

It is evident from previous studies (16, 8, 15, 5) that the stability of the intramolecular hydrogen bond and the relatively inert basic functions of the carbonyl groups of the keto form renders the equilibrium in acetylacetone particularly insensitive to displacement by solvent interaction. The results of Bernstein and Powling (5) show that even in acids and basic oxygen-containing compounds the perturbation of the equilibrium can be explained with only small extensions of the Kirkwood-Onsager theory, involving the stabilization of one isomer with respect to the other on the basis of its dielectric environment. In order to determine the extent of specificity in the interaction between solvent and acetylacetone the semiempirical extension of the Kirkwood-Onsager (13, 17) model for polar solvents, used by Bernstein and Powling (5), is utilized to calculate

the equilibrium at infinite dilution; this will be compared with the infinite dilution values obtained in this study.

The free energy change at 25° C. is directly proportional to the solvent property $(\epsilon - 1)/(2\epsilon + 1) \times \rho/M$, (ϵ = dielectric constant, M = molecular weight, ρ = density at 25° C. of the solvent (5)). Inert solvents and weak acids extrapolate at $\epsilon = 1$ to the gas value of $-\Delta F$, but basic compounds extrapolate to a slightly higher value (0.2–0.3 kcal.). In the present calculations the appropriate correlation in the work of Bernstein and Powling (5) was chosen to compute $[\text{enol}]/[\text{keto}]$ at 25° C. for each solvent, at high dilution.

Table VIII shows the agreement obtained between the computed and measured mole percentage of each component at infinite dilution in the four solvents.

TABLE VIII
COMPUTED AND MEASURED EQUILIBRIUM BETWEEN KETO AND ENOL
FORMS OF ACETYLACETONE IN VARIOUS SOLVENTS AT HIGH DILUTIONS

Solvent	Mole % keto computed (5)	Mole % keto extrapolated from NMR intensity measurements to infinite dilution
Cyclohexane	12.1	~ 9
Acetic acid	23.6	~26
Pyrrole { as a base as an acid	{ 11.0 20.0 }	~42
Triethylamine	6.4	0

According to Table VIII, cyclohexane and acetic acid behave as non-interacting solvents and this has been confirmed here, since there is no change in relative chemical shifts throughout the concentration range (Tables IV and VII). The agreement between computed and measured equilibrium constants obtained for triethylamine is quite good considering all the approximations involved. It was found however that even in very dilute solutions the keto form did not appear, so that in this case the infinite dilution equilibrium constant is not a valid test of interaction. Considered either as an acid or as a base, pyrrole does not give good enough agreement to be considered as an inert solvent.

It must be pointed out here that the "experimentally measured" equilibrium at infinite dilution is available only after appreciable extrapolation. Any interaction which occurred however in dilute solution would influence the chemical shift measurements in this region and these have not been found to show any anomalies.

4. Solutions of Acetylacetone in Acetic Acid

In solutions with acetic acid the —OH signals are broadened at room temperature owing to partial proton exchange (19). The extrapolation of the chemical shifts of the —OH protons is made from 0.3 mole fraction acetylacetone to infinite dilution because the signals cannot be detected in dilute solution. Since, however, the correlation between the dielectric constant of acetic acid and the free energy of enolization holds in dilute solutions of acetylacetone in acetic acid, it is presumed that the extrapolation of the chemical shifts of the —OH groups is justified. There is no evidence that acetic acid interacts with acetylacetone in solution; it remains as dimers throughout the concentration range accessible to measurement.

It is interesting to contrast the results in acetylacetone with the dilution shifts of the acetic acid hydroxyl group in acetone which suggests a complex of the monomer acetic

acid with acetone in dilute solution (11). The interpretation of a lack of such complexing in acetylacetone must rest on the basis of a low concentration of keto form (27 mole % at infinite dilution) which is unable to compete with the hydrogen bonds in dimeric acetic acid. There will also be no tendency to interact with the very stable intramolecular hydrogen bond in the enol form.

5. Solutions of Acetylacetone in Cyclohexane

It is of considerable interest that mixtures of acetylacetone with cyclohexane give the same chemical shifts at infinite dilution of either component. There are therefore no interactions (through hydrogen bonds or otherwise) of the types, enol-enol, enol-keto, or keto-keto in acetylacetone. The keto-enol equilibrium is however somewhat shifted owing to the change in dielectric constant resulting from dilution with cyclohexane.

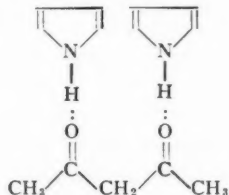
6. The PMR Spectrum of Pyrrole

The spectrum of pyrrole has not been successfully assigned but it is resolved here into two quartettes, which overlap in the pure liquid. There is considerable self-association in pyrrole (14, 21, 22, 9), the nature of which is still not clear. The two alternatives are π -association, studied recently by Reeves and Schneider (18), and conventional hydrogen bonding. Evidence for polymeric associations is fairly convincing (22). Dilution of pyrrole causes the high field quartette to move further to high field, and since this is a small shift 4-5 cycles in cyclohexane, it is interpreted as a secondary effect of breaking the self-association and isolation of monomer pyrrole molecules. The second (low field signal) does not change its chemical shift with respect to the internal cyclohexane reference.

The nitrogen quadrupole causes the —N—H proton resonance to broaden out below the noise level in both pure pyrrole and cyclohexane solutions. This precludes a study of internal association in pyrrole directly.

7. Interactions in Solutions of Acetylacetone in Pyrrole

A broad —NH proton resonance of pyrrole is detectable in acetylacetone and by extrapolation it should appear 42 cycles to the low field side of the low field —CH= signals, if the nitrogen quadrupole was decoupled. Examination of Table III, in conjunction with the freezing diagram, indicates complex formation in the binary system, with preference for 2:1 pyrrole-acetylacetone associations. The large change in chemical shift observed in the N—H proton and smaller change in the keto —CH₂— (19 c./s.) show the breaking of self-association in pyrrole and formation of a complex through the —NH proton, but affecting the keto —CH₂— only as a secondary perturbation. The protons of the pyrrole nucleus are also affected (20 c./s.), as might be expected. The only reasonable explanation of these facts is an association via the —NH and carbonyl oxygens of the keto form. There are thus 1:1 and 2:1 complexes possible in solution according as one or both carbonyl groups are affected.



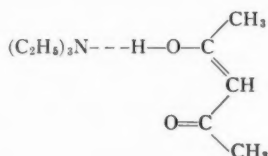
The chemical shift of the —CH₂— group relative to the CH₃— in the keto form can be understood as a doubling of the secondary effect of association in the —CH₂—

group, since two pyrrole molecules are involved on the same molecule at infinite dilution. In forming this complex the —NH signal is moved 114 c./s. to low field. The interpretation of this in terms of complex stability is ruled out because of the self-association, which occurs in pyrrole itself. There is evidence for a similar type of association with pyrrole and acetone (20). The freezing diagram in the acetone-pyrrole system showed 1:1 complex presumably formed via the —NH and carbonyl groups.*

The preference for a complex formation with the keto form explains the much higher concentration of this component than might be expected from (Table VII) a non-interacting solvent with the dielectric constant of pyrrole.

8. Interactions in Solutions of Acetylacetone in Triethylamine

The absence of any keto form in solutions with triethylamine, together with a very large dilution shift of the enolic —OH proton, implies enolization followed by specific interaction of the nitrogen lone pair with the enolic proton (Table VI, Fig. 9). In view of the stability of the intramolecularly hydrogen bonded ring, the lone pair on the nitrogen does not successfully compete with the internal bond until triethylamine exceeds 50 mole % (Fig. 9). The freezing diagram suggests a 1:1 and 1:2 complex formation, and in view of the proton resonance experiments the 1:1 has the structure:



It is not so easy to account for 1:2 associations unless the enol ring is broken on a second molecule.

In the 1:1 complex the symmetry of the enol methyl groups is destroyed and they should become magnetically non-equivalent. A 10 mole % solution of acetylacetone in triethylamine was investigated for the methyl proton resonance. Splitting of approximately 1/2 c./s. was observed, but since this is about as much as can be resolved, the experiment is not conclusive. This does not however detract from the interpretation of the interaction, since complete complexing of the acetylacetone does not occur until solutions are extremely dilute (Fig. 9), and even with complete complexing, possible proton exchange processes may average out the methyl resonances.

The change in chemical shift of the enol —OH proton (Fig. 9) is exceptionally large. This change is the composite effect of the breaking of the internal hydrogen bond and the formation of hydrogen bonded complex to the triethylamine. The first effect will cause the signal to move to high field, the second to low field. The experimental results indicate an unusually large shift to high field. Such an observation is consistent with fast exchange between free and complexed enolic —OH groups.

ACKNOWLEDGMENTS

The author wishes to express his appreciation of discussions with Dr. W. G. Schneider and to thank Mr. Yves Lupien for carrying out the experiments on freezing points in these systems.

*The freezing diagram in this system was kindly supplied by Mr. Yves Lupien.

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RAMAN SPECTRA AND CONFIGURATION OF SOME α -FURYL AND α -BENZOFURYL KETOXIMES¹

F. DULLIEN

ABSTRACT

Raman spectra of α -furyl and α -benzofuryl ketoximes were taken and analyzed. It was found that the values of the CN frequencies of the isomers display regular differences. By assuming in the *syn* isomers a weak hydrogen bonding between the OH oxygen and the ring hydrogen, which results in an increased localization of the unbonded electron pair of the OH oxygen and, as a consequence, a decreased resonance with the ring, these differences could be interpreted in agreement with chemical experience.

INTRODUCTION

In only a very few cases involving symmetrical molecules containing a limited number of atoms could Raman spectra so far be successfully used to establish the configuration of *cis-trans* isomers. In the few instances known, the number of lines and their state of polarization were used. To the best of our knowledge there is only one work to be found in the literature dealing with assignment of configuration to stereoisomeric oximes that uses Raman spectra of the compounds concerned (1). This approach was based on a comparison with Raman spectra of "analogous" isomeric ethylene derivatives, and the conclusion reached in this work was in complete disagreement with all experience gained in this field by other methods.

The only physical method to yield satisfactory results with oximes so far appears to be the measurement of the electric moments (2, 3). As some isomeric oximes had become available to us in a high state of purity, efforts were made to take Raman spectra and to draw conclusions as to the configuration and fine structure of the isomers.

EXPERIMENTAL

The following isomeric compounds were examined: methyl- α -furyl ketoximes (m.p. 74° and 104° C.); ethyl- α -furyl ketoximes (m.p. 73° and 78° C.); phenyl- α -furyl ketoximes (m.p. 149° and 164° C.); methyl- α -(5-methylfuryl) ketoximes (m.p. 83° and 110° C.); methyl- α -benzofuryl ketoximes (m.p. 154 and 161° C.); and phenyl- α -benzofuryl ketoximes (m.p. 145° and 156° C.). The compounds were prepared in a high state of purity by Mr. Gyorgy Ocskay in the course of his work towards obtaining the degree of Candidate of Chemical Sciences.

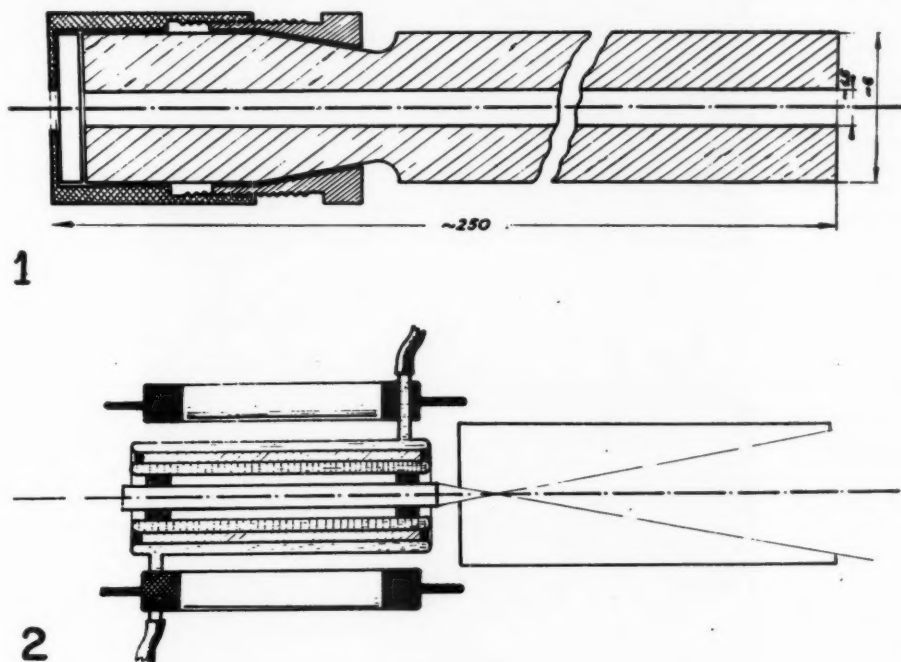
The substances rapidly discolored on standing and had to be purified immediately prior to examination. The compounds were dissolved in hot ethanol, some active carbon was added, and then the compounds were filtered, first through paper filter and then a biological glass filter. Precipitation was brought about by adding water to the filtrates, then the compounds were filtered on a suction filter and dried in a vacuum desiccator. They appeared white after purification; their solution, however, always had a slight yellowish tint, darkening rapidly on standing. The compounds decomposed and discolored on melting, and since no adequate equipment for examination of powders was available, only the solution technique could be used. To permit tolerable exposures, however, solutions of high concentrations were required.

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Private contribution. This work was completed at the Institute of Physical Chemistry, Technical University, Budapest, Hungary.

After experimenting with numerous solvents, pyridine was found to be the most adequate one. In fact, this solvent displayed an extraordinary dissolving power for all derivatives examined. It was rather surprising to find that benzene had a similar dissolving power for methyl- α -furyl ketoximes, m.p. 74°C ., both ethyl- α -furyl ketoximes, and methyl- α -(5-methylfuryl) ketoxime, m.p. 83°C . The rest of the compounds dissolved only slightly in benzene.

As only a few tenths of a gram of each compound was available, the exposures were taken by using the capillary microtechnique described elsewhere (4). The liquid under examination was sucked into a long, narrow capillary (see Fig. 1), which afterwards



FIGS. 1 and 2.

was sealed by a small, round, glass window (as shown in the figure) providing a very strong, air-tight seal. The capillary Raman tube was held in position with the aid of hard rubber rings in the center of a glass tube system forming four jackets (see Fig. 2). The capillary is surrounded immediately by an air jacket; then follow two filter jackets and a cooling water jacket, in this order. The jacket system, forming a self-contained unit, is accommodated in a lamp housing containing four Hanau Type S500 mercury vapor lamps (see Fig. 3). The lamp housing is provided with inside mirror surfaces and water jackets. Our experiences regarding the most efficient exploitation of the luminous flux of the mercury vapor lamps being in agreement with those of other authors (5), the closest packed arrangement of lamps, Raman tube, and mirrors possible was strived at in the construction of the lamp housing. Provided only a closely packed arrange-



FIG. 3.

ment can be secured, the use of elliptical mirrors appears to be out of place, not even the principle of conjugated foci being of any use in case of strong filtration. Precision alignment of the Raman tube was done by the aid of a support, permitting two independent displacements of the lamp housing both in the vertical and in the horizontal plane. The lamp housing was set as close to the slit as possible, and the exit end of the Raman tube was right at the slit of the spectrograph. As has been shown elsewhere (4), under the given set of conditions, including exposures, the same quality of Raman spectra can be obtained as when using Raman tubes of whatever large cross sectional area and/or any system of condensing lenses, provided the index of refraction of the liquid under examination is at least slightly higher than that of the Raman tube. Since the compounds under examination assumed a yellowish tint to varying degree, some of them

could be examined with both 4358 and 5461 Å excitation, whereas for the majority of them only 5461 Å excitation could be used. No rare earth salts being available, continuous background was suppressed by using a carbon tetrachloride solution of iodine and a solution of malachite green in pyridine, in the case of 4358 and 5461 Å excitation, respectively. The ultraviolet region of the spectra was removed by a 1:10 solution of nitrobenzene in ethanol.

Under such conditions, using exposures ranging from 3 to 7 hours and a Zeiss spectrograph with a set of three prisms and a 80-cm. focal length camera (relative aperture 1:17), fairly incomplete spectra were obtained. Spectra were photographed on Agfa Gelb Rapid and Agfa Rot Rapid plates. The spectrum of the iron arc was photographed beside every Raman spectrum by using a slit diaphragm and a total reflection prism in front of the slit. Although greatest care was exercised throughout all these operations, minor displacements, to be corrected for in the course of the evaluation of the spectra, could never be prevented. The solutions were filtered prior to examination by sucking them through a biological glass filter and yielded, as checked with the aid of a nephelometer, fairly clear liquids. The temperature of the solution never exceeded 40° C. during the exposures.

Plates were developed for 4 minutes at 18° C. in D19 Developer. Spectra were measured with a densitometer. The maximum density reading was accepted as the location of the line. The wave lengths of the Raman lines were found by interpolation between close lying iron lines. The precision of the individual readings being, in general, ± 0.01 mm., a precision of about ± 1 cm.⁻¹ follows for the value of the Raman frequencies, if the linear dispersion of 20–25 Å/mm. is considered. The above-mentioned displacements between iron arc and Raman spectra were corrected for with the aid of the weak mercury lines appearing in the Raman spectra. As a check on the accuracy of the measurements, the known wave lengths of these mercury lines could be found, by interpolation between lines of the iron arc and using a series of mercury spectra taken with extraordinary care, to one tenth of an Angstrom.

The experimental results are shown in Table I.

RESULTS AND DISCUSSION

In the case of the α -furyl derivatives the highest frequency could invariably be assigned to the CN bond, with the only exception of 1701 cm.⁻¹, found in the case of the pyridine solution of the 78° C. m.p. ethyl- α -furyl ketoxime, which could not be assigned to any vibration of the molecule. This assignment is in agreement with what appears to be a well-established experience, i.e., that the value of this frequency is about 1650–1660 cm.⁻¹ and 1655–1665 cm.⁻¹, in aliphatic aldoximes and ketoximes, respectively, whereas it is about 30 wave number units less in the aromatic oximes (1, 7, 8, 9). The rest of the frequencies found in the spectra of these derivatives could be assigned to vibrations of the furane ring, by way of comparison with the infrared and Raman spectra of furane and various derivatives (10, 11).

Since other authors invariably found only one line in the 1560–1590 cm.⁻¹ range, it is most likely that one of the two lines found in some of our spectra is due to the solvent. This is supported by the fact that strong lines were found at 1577 and 1583 cm.⁻¹, in the spectra of pyridine and benzene, respectively, taken under conditions identical with those of the experiments. (For sake of easier comparison these values are measured from the mercury line 5461 Å.) Owing to the overlapping of lines, however, it could not in

TABLE I

Compound	M.p.	Solvent							
Methyl- α -furyl ketoxime	74° C.	Benzene							
	(<i>syn</i>)	Pyridine	1635(s) ^{††}	1583(m) ^{††}	1566(m) ^{††}	1479(vs) ^{††}	1428(w)	1376(w) ^{††}	
	104° C.	Pyridine	1628(s) [*]	1577(m) ^{††}		1480(vs)		1374(vw)	
Ethyl- α -furyl ketoxime			1619(s) ^{††}		1574(vs) ^{††}	1492(vs) ^{††}		1384(vw) ^{††}	
	78° C.	Benzene	1636(s) [*]						
	(<i>syn</i>)	Pyridine	1624(m) [*]		1563(w)	1479(vw)		1272(vw)	
	73° C.	Benzene	1624(m) [*]			1481(s)			
	(<i>anti</i>)	Pyridine	1617(s) [*]	1606(w) ^{††}		1490(s)			
Methyl- α -(5-methyl-furyl) ketoxime	110° C.	Pyridine	1626(m) [*]		1573(vs)	1492(vs)			
	(<i>syn</i>)				1525(s)				
	83° C.	Benzene	1623(s) [*]						
Phenyl- α -furyl ketoxime			1618(s) [*]		1583(m) ^{††}				
	(<i>anti</i>)	Pyridine			1546(vs)				
	149° C.	Pyridine	1595(m) [*]		1544(vs)	1476(s)			
	(<i>syn</i>)				1580(m)				
Methyl- α -benzofuryl ketoxime	161° C.	Pyridine	1595(s) [*]		1572(s)	1492(vs)		1381(w)	
	(<i>anti</i>)								
	161° C.	Pyridine							
Phenyl- α -benzofuryl ketoxime	154° C.	Pyridine	1590(m) [*]		1556(vs)		1448(m)	1255(s)	
	(<i>anti</i>)				1569(vs)		1441(w)		
	145° C.	Pyridine							
Phenyl- α -benzofuryl ketoxime	156° C.	Pyridine			1554(vs)	1494(vw)	1446(m)		
	(<i>syn</i>)								
	156° C.	Pyridine	1590(s) [*]		1562(vs)		1447(w)		

*Denotes CN frequency.

†Denotes both Hg e and Hg c excitation; in the rest of the cases there was only Hg c excitation.

‡Denotes solvent frequency.

each case be established with certainty whether a line in this range was to be assigned to the substance investigated or to the solvent.

Those frequencies of the benzofuryl derivatives which could be measured accurately were unequivocally assigned to the vibrations of the coumarone skeleton (12). It is most likely that the CN frequency appears around 1590 cm^{-1} in the form of a shoulder in one of the isomers, whereas in the other one the very strong coumarone frequency at 1610 cm^{-1} apparently completely covers it.

The chief problem involved in the present investigation being the establishment of the configuration of each of the two different types of isomers, our attention had to be focused on the CN frequency, partly because this was the only one that could be identified with a fair degree of certainty, and partly because it was assumed *a priori* that variations of this frequency could be interpreted in terms of structural differences, in the most reliable manner.

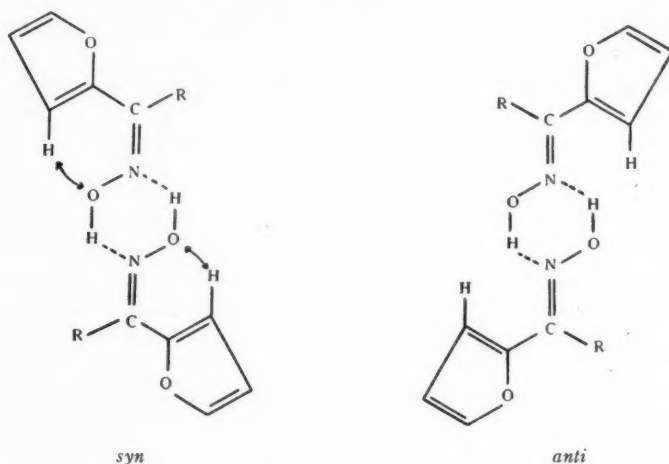
As is apparent from Table I, in the case of the alkyl-aryl ketoximes the CN frequencies of the isomers display regular differences. In the following discussion an attempt is made to account for these differences in terms of the different configurations. According to Stuart (15) the energy difference of *cis-trans* isomers is due partly to van der Waals forces acting between the substituents and partly to interaction between the substituents and the double bond. In the spectra this energy difference is displayed in the value of the double bond frequencies of the isomers, these being, in accordance with expectation, higher in the more stable modification in the case of both the dimethyl ethylene and the dichloro ethylene isomers (16), the only cases which appear to have been recorded in the literature.

It appears rather obvious, then, that similar differences might arise in the case of oximes too, if only the steric conditions permit an interaction between the substituents. The fact that in the case of aliphatic oximes only one CN frequency has invariably been found (7), accordingly, might be due to lack of interaction between the substituents in either isomer, owing to unfavorable steric conditions. In the case of the alkyl- α -furyl ketoximes, however, in one of the isomers (*syn*) there can be an interaction between the furane ring and the OH group, if it is supposed that the molecule is practically coplanar. Coplanarity, however, is rendered very probable by finding in all aromatic oximes diminished CN frequencies, obviously brought about by conjugation (13).*

In discussing the nature of the assumed interaction, the fundamental question appears to be whether the hydrogen or the oxygen of the OH group should be responsible for it. Information on this point can be obtained from the results gained by Calderbank and Le Fèvre (2), who measured the electric moments of isomeric benzaldoximes and furaldoximes. These authors calculated the maximum and minimum values of the dipole moments and found the measured values in close proximity to the minimum ones. As the latter corresponds to the case when the OH hydrogen points away from the ring (in the *syn* derivative), these results apparently prove that the OH hydrogen cannot

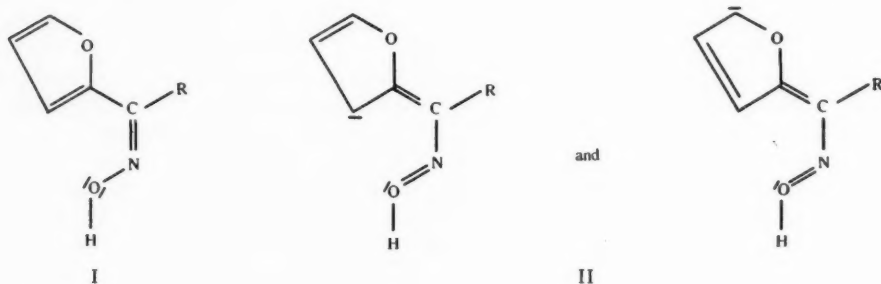
*Ramart-Lucas, however, gave a different interpretation of the ultraviolet absorption spectra of α -furyl ketoximes. On finding unchanged conjugation in tertiary butyl- α -furyl ketoxime, she came to the conclusion that the carbon atoms in furane should have a tetragonal structure. We think, however, that a much more obvious explanation for the phenomenon observed by Ramart-Lucas should be that in the molecule examined by her the tertiary butyl group does not interfere with the coplanar structure, which could be confirmed by model experiments. This interpretation is further supported by other findings of Ramart-Lucas, i.e. that conjugation in the oxime of α -trimethyl acetothienone is considerably diminished. This, in our opinion, is the consequence of the larger atomic radius of sulphur as compared with that of oxygen. Consequently, in the reasoning to follow it will be assumed that α -furyl ketoximes possess practically coplanar structure.

play a role in the interaction. It is further in support of this view that under the conditions of the present investigations, in the benzene solutions, the oximes were, in all probability, in a highly dimerized state where the OH hydrogens should be rendered ineffective to any other sort of interaction. Considering all these facts it is most likely that in the *syn* derivative there is a hydrogen-bond-like interaction between the OH oxygen and a hydrogen in the ring:



The possibility of a similar hydrogen bonding has been assumed by others (17). To see the influence such hydrogen bonding exerts on the value of the CN frequency first the nature of the conjugation in the molecule should be considered.

It is most likely that the unbonded electron pair of the OH oxygen and the π -electron system of the molecule enter into resonance that can be represented by the following mesomeric forms:

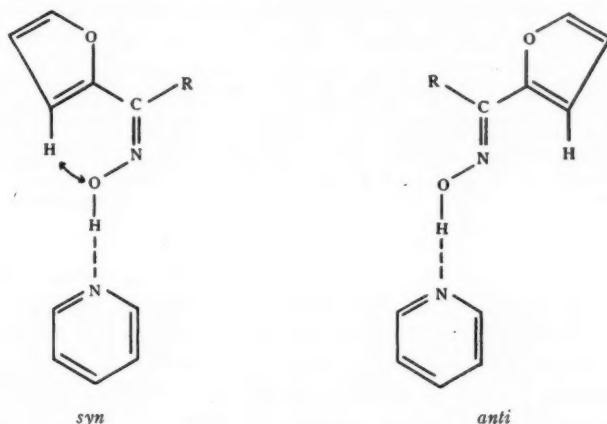


It should be noted that the probability of forms II is presumably very small. The mesomeric form analogous to II has been assumed by Reiser and co-workers (18) to account for the smaller electric moments measured with aromatic etoximes as compared with those of the aliphatic ones. Now, if it is considered that by assuming a hydrogen-bond-like effect on the OH oxygen, its unbonded electron pair should be somewhat localized and result in a diminished probability of forms II, the final conclusion as to the con-

figuration of the isomers obviously is that higher CN frequency should be displayed by the *syn* derivatives than by the *anti* ones, and that is in agreement with chemical experience.

At last, it should be pointed out that the results obtained on the oximes in pyridine solution are also in support of the assumed nature of conjugation in the α -furyl ketoximes.

As is apparent from Table I, here the CN frequencies are invariably lower than in the case of the benzene solutions. Purely qualitatively this may be brought about by the strong solvent action of pyridine, i.e. by the latter breaking up the dimers and itself entering into hydrogen bond with the oxime, an assumption supported by the extraordinary solubility in pyridine of all the oximes examined. Consequently, this should be an appreciably stronger interaction than the dimerization of oximes and, on the other hand, it should also be qualitatively different from the latter, involving only the OH oxygen and leaving the nitrogen (or less likely the oxygen) unaffected.*



Stronger hydrogen bonding of the OH hydrogen, however, should obviously encourage conjugation, i.e. the probability of forms II increases, resulting, in turn, in a lower CN frequency. Thus, by assuming in the *syn* isomers a weak hydrogen bonding between the OH oxygen and the ring hydrogen in the ortho position, resulting in an increased localization of the unbonded electron pair of the OH oxygen and, as a consequence, a decreased resonance with the ring, the observed differences in the CN frequencies of the three alkyl- α -furyl ketoximes examined could be interpreted in agreement with chemical experience. The still lower CN frequencies found in the rest of the compounds are obviously due to increased conjugation, whereas the reason for having identical CN frequencies in the two phenyl- α -furyl ketoximes, in all probability, is the lack of any difference between the two isomers as far as the interaction between the OH oxygen and the ring hydrogen is concerned.

*Kahovec and Kohlrausch (1) assumed that either the association of oximes with hydrogen bond on the oxime nitrogen or the high electron affinity of the oxime oxygen by means of which it should suck π -electrons out of the double bond, or both, should result in lower CN frequencies. These assumptions, however, are inconsistent with the results of the present experiments. Since, if the association of the oximes lowered the CN frequency by a mechanism assumed by these authors, one would expect an increased CN frequency in pyridine as a consequence of the splitting up of the dimers and the oxime nitrogen becoming free. Similar applies to the other alternative explanation, let alone that it appears a priori more likely that the oxime oxygen affects the charge distribution in a sense opposite to what was assumed by the authors.

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NOTES

1,1-DISUBSTITUTED-2-NITROGUANIDINES

A. F. MCKAY AND P. R. STEYERMARK

A large number of nitroguanidine derivatives have been prepared by the reaction of primary amines with 1-methyl-1-nitroso-2-nitroguanidine (3, 4, 5) but only a few compounds derived from secondary amines have been described. These latter products are 1,1-dimethyl-2-nitroguanidine (4), 1-morpholinyl-2-nitroguanidine (2), and 1-piperidyl-2-nitroguanidine (2). It was known (4) that other secondary amines such as diethylamine and di-*n*-propylamine would combine with methylnitrosanitroguanidine but no nitroguanidine derivatives were isolated from the reactions. Since all prior evidence indicated that secondary amines should give nitroguanidine derivatives, this reaction was reinvestigated.

The 1,1-disubstituted-2-nitroguanidines prepared by the reaction of secondary amines with methylnitrosanitroguanidine are difficult to isolate and purify. The reaction products were generally oils from which the desired product had to be extracted with a suitable solvent. The details are described below for the preparation of 1,1-dicyclohexyl-2-nitroguanidine and 1-pyrrolidyl-2-nitroguanidine (1).

EXPERIMENTAL

1,1-Dicyclohexyl-2-nitroguanidine

A solution of dicyclohexylamine (4.9 g., 0.027 mole) in 50% aqueous ethanol (50 cc.) was added to a stirred suspension of 1-methyl-1-nitroso-2-nitroguanidine (3.94 g., 0.027 mole) in ethanol (10 cc.) at room temperature. The stirring was continued for 6 hours after which the reaction mixture was allowed to stand for 72 hours at room temperature. The supernatant liquid was poured off and the residue was extracted with benzene (50 cc.) and ethyl acetate (80 cc.). After the combined supernatant and extracts were concentrated to a volume of 35 cc., the solution was dried over anhydrous sodium sulphate and diluted with petroleum ether (250 cc.). Large rhombic crystals (m.p. 140–170° C.) separated from the solution when it was left in the refrigerator over a period of 5 days, yield 4.82 g. (68%). Four crystallizations from acetone – petroleum ether solvent raised the melting point to a constant value of 152° C. with decomposition. Calculated for $C_{13}H_{24}N_4O_2$: C, 58.20; H, 9.02; N, 20.88%. Found: C, 58.51; H, 8.85; N, 20.83%.

1-Pyrrolidyl-2-nitroguanidine

A mixture of 1-methyl-1-nitroso-2-nitroguanidine (5.74 g., 0.04 mole) and pyrrolidine (2.9 g., 0.04 mole) in water (25 cc.) was stirred for 1 hour at room temperature. The white precipitate was collected by filtration and the filtrate was extracted with nitromethane (3×50 cc.). After the nitromethane extract was evaporated under reduced pressure to dryness, the residue was dissolved in petroleum ether. The petroleum ether solution on cooling deposited more crystals. The two crops of crystals (m.p. 184–185° C.) weighed 1.40 g. (23%). Three crystallizations from acetone – petroleum ether solution raised the melting point to 189–190° C. Fishbein and Gallagher (1) report a melting point of 189–190° C. for 1-pyrrolidyl-2-nitroguanidine.

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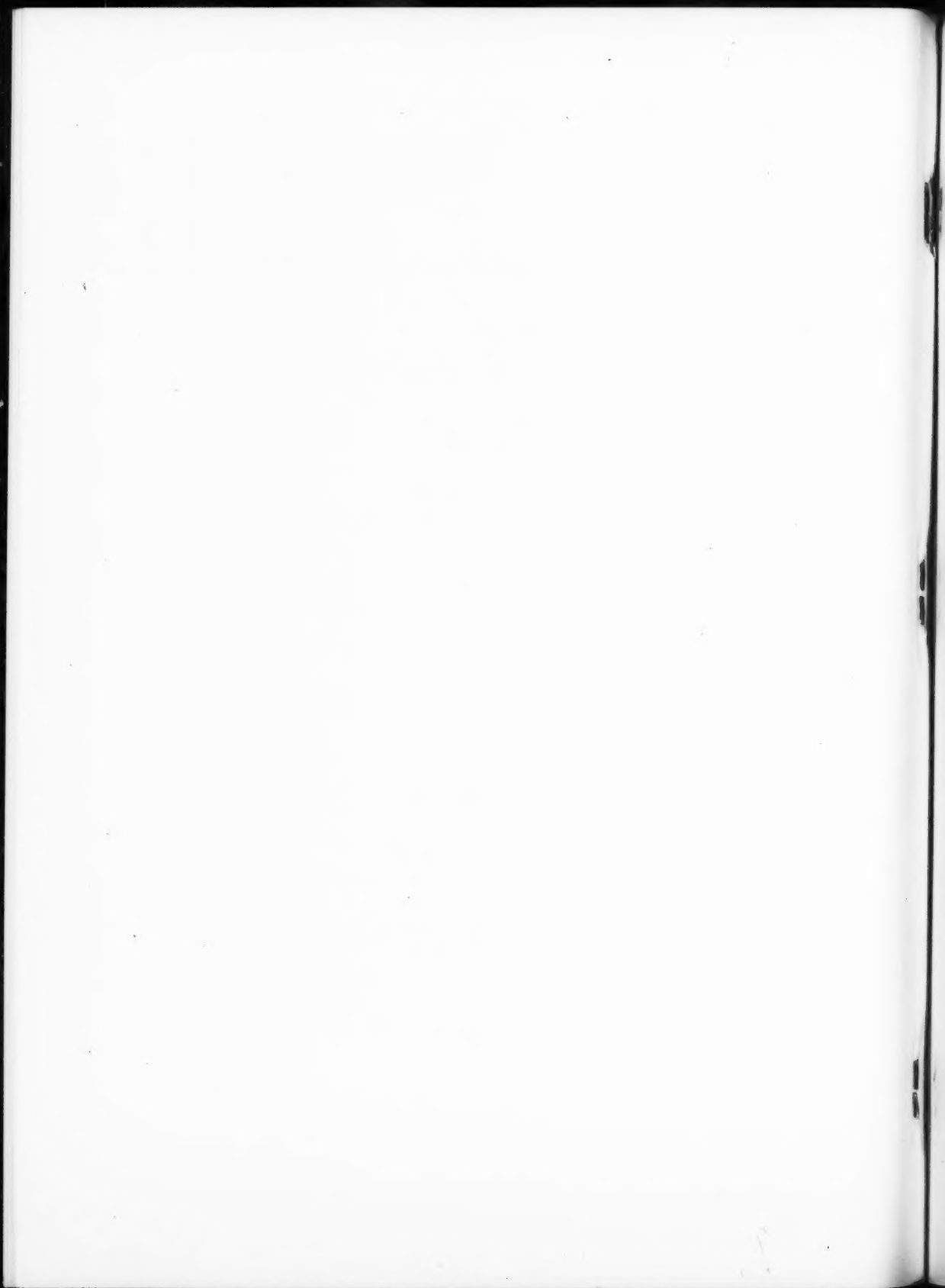
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Contents

	Page
The Effect of Hydrogen Chloride on the Infrared Spectrum of Nylon— <i>P. Larose</i>	1239
Cinétique de l'hydrolyse de l'adénosine triphosphate en solution alcaline— <i>A. M. Couture and Ludovic Ouellet</i>	1248
Voltaic Cells in Fused Salts. Part II. The Systems: (a) Silver—Silver Chloride, Lead—Lead Chloride; (b) Silver—Silver Chloride, Zinc—Zinc Chloride; and (c) Silver—Silver Chloride, Nickel—Nickelous Chloride— <i>S. N. Flengas and T. R. Ingraham</i>	1254
Preparation of Guanidine from Ammonium Thiocyanate, Sulphur Dioxide, and Ammonia under Pressure— <i>Jean L. Boivin and Meude Tremblay</i>	1260
Photo-initiated Free Radical Polymerization of Methyl Acrylate in Aqueous Solution— <i>C. Chaitanyan Menon and M. Santappa</i>	1267
Determination of Lead by Dithizone in a Single Phase Water-Acetone System — <i>D. G. M. Diaper and A. Kuksis</i>	1278
The Reaction of Acetic and Trifluoroacetic Anhydrides with Some Substituted Guanidine Hydrochlorides— <i>W. F. Cockburn and R. A. B. Bannard</i>	1285
An Ionization Gauge Detector for Gas Chromatography— <i>S. A. Ryce and W. A. Bryce</i>	1293
The Reaction of Active Nitrogen with Hydrogen Chloride— <i>D. M. Wiles and C. A. Winkler</i>	1298
Reduction of Halogenated Nitrobenzenes— <i>Paul E. Gagnon, Karl F. Keir- stead, and Brian T. Newbold</i>	1304
Solvolysis in Hydrogen and Deuterium Oxide. II. Strongly Solvated Substrates — <i>R. E. Robertson and P. M. Laughton</i>	1319
Dielectric Constants of Liquid Sulphur Dioxide, Ethyl Chloride, and Ethylene Oxide— <i>J. D. Nickerson and R. McIntosh</i>	1325
The Solubility of Malachite— <i>J. F. Scaife</i>	1332
Kinetics of the Photochlorination of Monochloromethyl Chloroformate in the Gas Phase— <i>M. J. Dignam, W. G. Forbes, and D. J. Le Roy</i>	1341
Nuclear Magnetic Resonance Measurements in Solutions of Acetylacetone. The Effect of Solvent Interactions on the Tautomeric Equilibrium— <i>L. W. Reeves</i>	1351
Raman Spectra and Configuration of Some α -Furyl and α -Benzofuryl Ketox- imes— <i>F. Dullien</i>	1366
Notes:	
1,1-Disubstituted-2-nitroguanidines— <i>A. F. McKay and P. R. Steyermark</i>	1375

